Supporting Information

Constructing Densely Functionalized Hajos–Parrish–type Ketones with Six Contiguous Stereogenic Centers and Two Quaternary Carbons in a formal [2 + 2 + 2] Cycloaddition Cascade.

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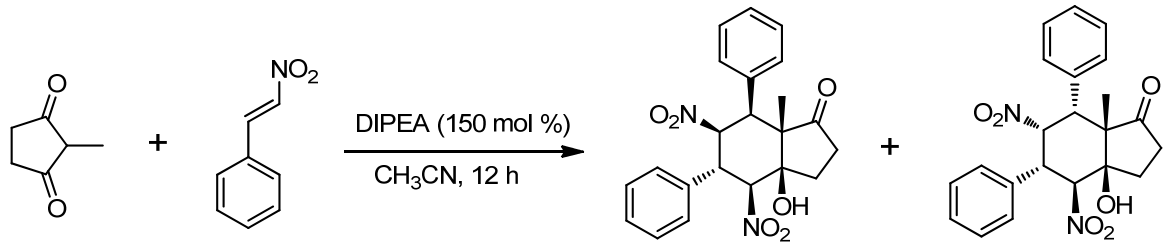
SUPPORTING INFORMATION (Contents**):**

General Procedure. All solvents were reagent grade. Reactions were normally carried out under nitrogen atmosphere in glassware. Merck silica gel 60 (particle size 0.04-0.063 mm) was employed for flash chromatography. Melting points are uncorrected. ^{1}H NMR spectra were obtained in $CDCl_3$ unless otherwise noted at 400 MHz (Bruker DPX-400) or 500 MHz (Varian-Unity INOVA-500). ^{13}C

NMR spectra were obtained at 100 MHz or 125 MHz. *E.e.* values were measured by HPLC on a chiral column (chiralpak IC, 0.46 cm ID x 25 cm, particle size 5 μ) by elution with THF-hexane. The flow rate of the indicated elution solvent is maintained at 1 mL/min, and the retention time of a compound is recorded accordingly. HPLC was equipped with the ultraviolet and refractive index detectors. The melting point was recorded on a melting point apparatus (MPA100 – Automated melting point system, Stanford Research Systems, Inc.) and is uncorrected.

Preparation of adduct 3a and 5a.



1 (1 equiv) **2a** (3.5 equiv) **3a** **5a**

To a solution of DIPEA (44 mg, 0.34 mmol, 1.5 equiv), 2-methyl-1,3-cyclopentanedione (**1**, 25 mg, 0.22 mmol) in CH_3CN (1.1 mL) was added nitrostyrene (**2a**, 116.3 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 12 h until the completion of the reaction, as monitored by TLC. Then the reaction mixture was directly filtered through a Celite bed (to remove insoluble polymer junk) and washed with EtOAc (15 mL). The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography with 20 % EtOAc–hexane to give **3a** (58.5 mg, 64% yield) as a pale yellow solid (R_f = 0.23 in 20% EtOAc–hexane developed two times on TLC) and **5a** (13.7 mg, 15%) as white solid (R_f = 0.19 in 20% EtOAc-hexane developed two times on TLC).

Select data for **3a**: m.p. 240–241 °C; IR (neat): 3441, 2919, 1740, 1556, 1454, 1364, 1073, 756, 701, 463 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6): δ 7.50 – 7.42 (m, 2 H), 7.40 – 7.32 (m, 4 H), 7.28 – 7.15 (m, 4 H), 5.93 (s, 1 H), 5.21 (d, J = 12.5 Hz, 1 H), 5.14 (dd, J = 12.5, 6.5 Hz, 1 H), 4.50 (t, J = 12.5 Hz, 1 H), 4.15 (d, J = 6.5 Hz, 1 H), 2.91 – 2.80 (m, 2 H), 2.76 – 2.68 (m, 1 H), 2.34 – 2.25 (m, 1 H), 0.96 (s, 3 H); ^{13}C NMR (125 MHz, acetone-d_6): δ 214.5 (C), 137.1 (C), 135.6 (C), 129.3 (6 CH), 128.94 (2 CH), 128.90 (2 CH), 92.7 (CH), 89.3 (CH), 79.8 (C), 58.0 (C), 50.2 (CH), 41.5 (CH), 34.1 (CH_2), 28.9 (CH_2), 19.3 (CH_3); MS (*m/z*, relative intensity): 410 (M^+, 18), 364 (15), 318 (52), 257 (81), 245 (45), 205 (21), 115 (51), 105 (35), 91 (100), 77 (34); exact mass calculated for $C_{22}H_{22}N_2O_6$ (M^+): 410.1478; found: 410.1477. Anal. Calcd for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83; O, 23.39; found: C, 64.45; H, 5.36; N, 6.56; O, 23.26.

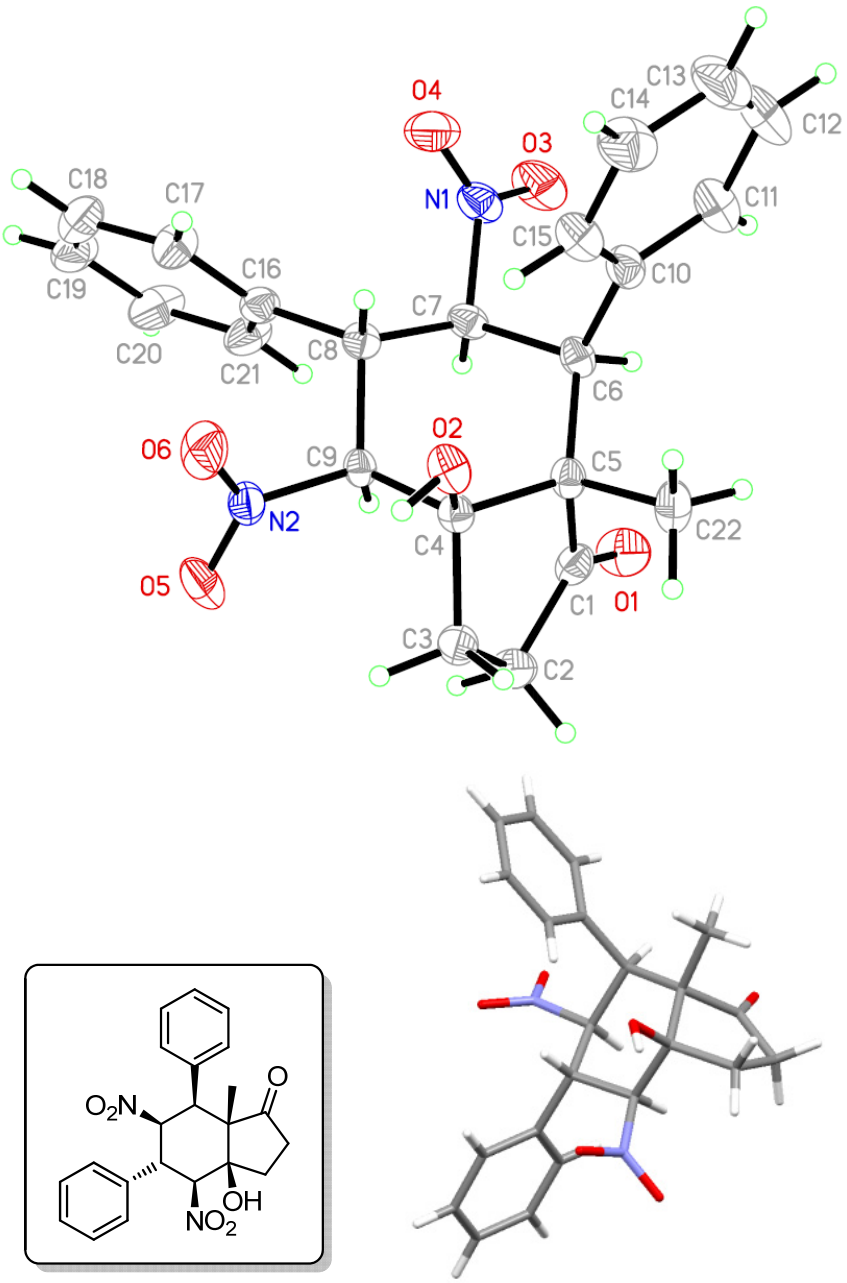


Figure S1. ORTEP and Stereo plots for X-ray crystal structures of (±)-**3a**.

CCDC 1474917 contains the supplementary crystallographic data for (±)-**3a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for (±)-**3a**.

Identification code	ic17001	
Empirical formula	C_{22} H_{22} N_2O_6	
Formula weight	410.42	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.4563(7) Å	a= 90°.
	b = 6.7710(4) Å	b= 93.8075(14)°.
	c = 25.4114(15) Å	g = 90°.
Volume	1966.8(2) $Å^3$	
Z	4	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	0.102 mm^{-1}	
F(000)	864	
Crystal size	0.40 x 0.27 x 0.05 mm^3	
Theta range for data collection	1.61 to 27.50°.	
Index ranges	-14<=h<=14, -8<=k<=8, -32<=l<=33	
Reflections collected	14689	
Independent reflections	4514 [R(int) = 0.0417]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9949 and 0.9604	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4514 / 0 / 273	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2sigma(I)]	R1 = 0.0586, wR2 = 0.1365	
R indices (all data)	R1 = 0.0758, wR2 = 0.1460	
Largest diff. peak and hole	0.394 and -0.209 $e.Å^{-3}$	

Select data for **5a**: m.p. 184–185 °C; ^{1}H NMR (500 MHz, acetone-d_6): δ 7.56 – 7.54 (m, 2 H), 7.37 – 7.30 (m, 2 H), 7.29 – 7.22 (m, 6 H), 6.18 (d, J = 13.0 Hz, 1 H), 5.47 (s, 1 H), 5.18 (dd, J = 4.5 Hz, 4.0 Hz, 1 H), 4.58 (dd, J = 12.5 Hz, 4.5 Hz, 1 H), 3.74 (d, J = 4.0 Hz, 1 H), 3.08 – 3.01 (m, 1 H), 2.79 – 2.75 (m, 1 H), 2.65 (dd, J = 19.0 Hz, 9.0 Hz, 1 H), 2.31 – 2.24 (m, 1 H), 1.11 (s, 3 H); ^{13}C NMR (125 MHz, acetone-d_6): δ 211.8 (C), 136.8 (C), 136.7 (C), 132.2 (2 CH), 129.9 (2 CH), 129.2 (CH), 128.9 (2 CH), 128.7 (CH), 128.0 (2 CH), 93.5 (CH), 87.5 (CH), 80.2 (C), 55.8 (C), 50.3 (CH), 44.1 (CH), 35.7 (CH_2), 28.8 (CH_2), 21.6 (CH_3).

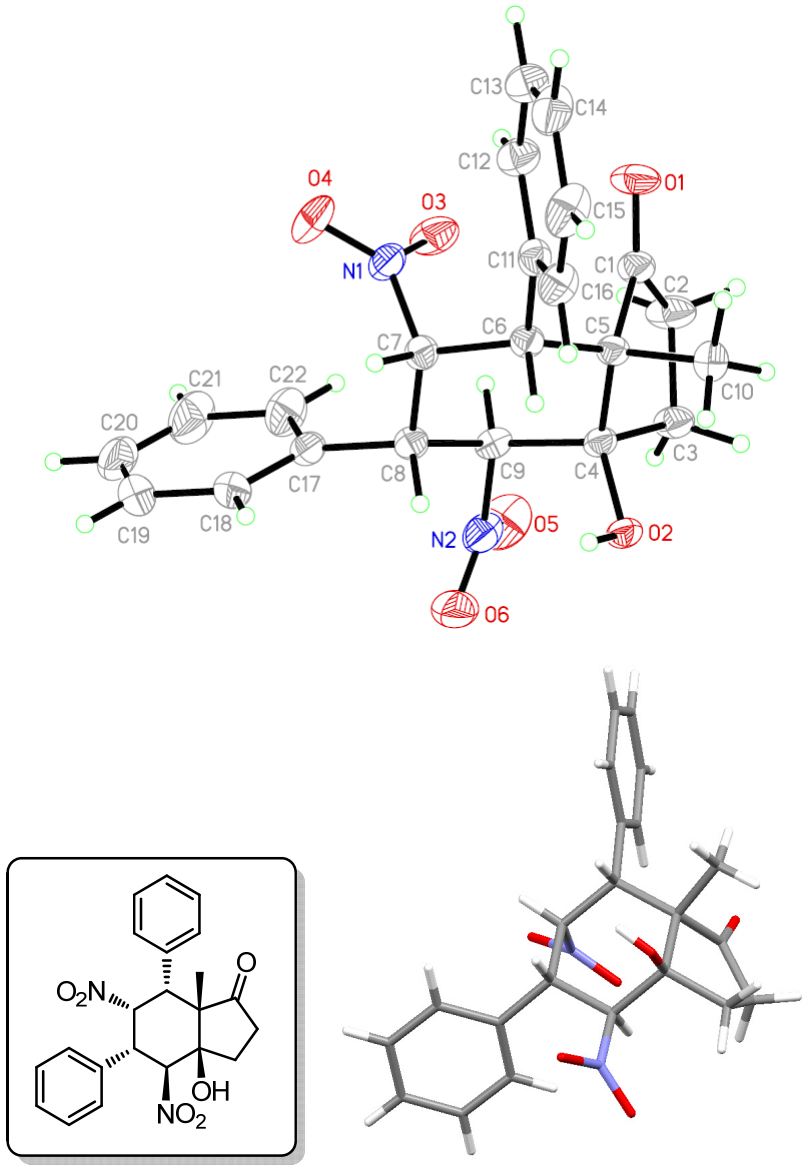


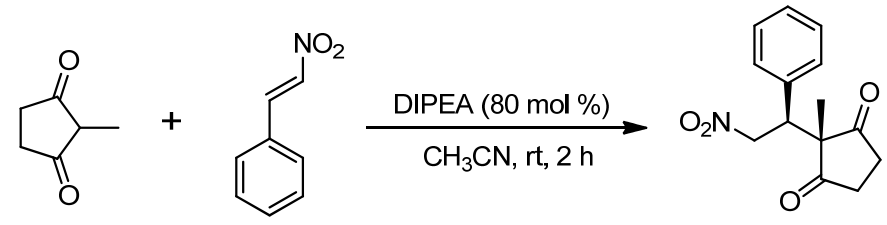
Figure S2. ORTEP and Stereo plots for X-ray crystal structures of (±)-**5a**.

CCDC 1495243 contains the supplementary crystallographic data for (±)-**5a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement for (±)-**5a**.

Identification code	ic18058-1	
Empirical formula	C22 H22 N2 O6	
Formula weight	410.41	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.60530(10) Å	a= 90°.
	b = 16.3208(3) Å	b= 90°.
	c = 18.4301(3) Å	g = 90°.
Volume	1986.83(6) $Å^3$	
Z	4	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	0.838 mm^{-1}	
F(000)	864	
Crystal size	0.506 x 0.150 x 0.065 mm^3	
Theta range for data collection	3.617 to 69.976°.	
Index ranges	-7<=h<=8, -16<=k<=19, -22<=l<=22	
Reflections collected	9468	
Independent reflections	3755 [R(int) = 0.0198]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5874	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3755 / 0 / 273	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0793	
R indices (all data)	R1 = 0.0326, wR2 = 0.0800	
Absolute structure parameter	0.52(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.151 and -0.225 $e.Å^{-3}$	

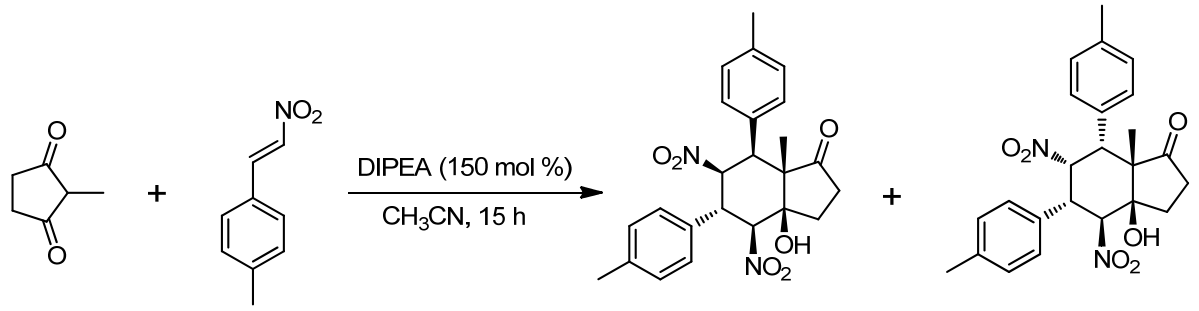
Isolation of the intermediate 4a.



1 (2 equiv) **2a** (1 equiv) **4a**

To a solution of DIPEA (62 mg, 0.48 mmol, 0.8 equiv), 2-methyl-1,3-cyclopentanedione (**1**, 135 mg, 1.20 mmol, 2 equiv) in CH_3CN (6 mL) was added nitrostyrene (**2a**, 90 mg, 0.60 mmol) and the resulting solution was stirred at room temperature for 2 h. The reaction mixture was concentrated *in vacuo* to give the residue. The crude product was purified by flash column chromatography with 10 to 20 % EtOAc–hexane (R_f = 0.29 in 25 % EtOAc–hexane) to afford product **4a** (35 mg, 22% yield) as a yellow oil. Selected data for **4a**: IR (neat): 3035, 2973, 2924, 1722, 1555, 1454, 1416, 1379, 1344, 1076, 799, 762, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28–7.23 (m, 3 H), 7.16 – 7.13 (m, 2 H), 5.04 (dd, J = 13.2, 9.6 Hz, 1 H), 4.95 (d, J = 13.2, 6.0 Hz, 1 H), 3.92 (dd, J =9.7, 6.0 Hz, 1 H), 2.72–2.51 (m, 2 H), 2.39–2.21 (m, 1 H), 2.10 – 1.90 (m, 1 H), 1.18 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 216.3 (C), 214.6 (C), 135.0 (C), 129.1 (2CH), 128.7 (2CH), 128.6 (CH), 74.8 (CH_2), 57.9 (C), 47.8 (CH), 35.5 (CH_2), 35.0 (CH_2), 19.4 (CH_3); MS (*m/z*, relative intensity): 261 (M^+, 1), 215 (4), 186 (20), 171 (21), 149 (58), 131 (100), 104 (71), 103 (47), 102 (69), 91 (100), 77 (64); exact mass calculated for $C_{14}H_{15}NO_4$ (M^+): 261.1001; found: 261.1003.

Preparation of adduct 3b and 5b.



1 (1 equiv) **2b** (3.5 equiv) **3b** **5b**

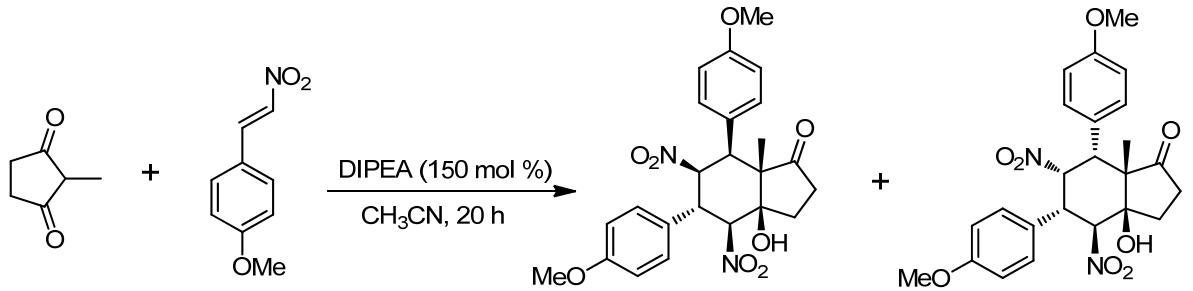
To a solution of DIPEA (44 mg, 0.34 mmol, 1.5 equiv), 2-methyl-1,3-cyclopentanedione (**1**, 25 mg, 0.22 mmol) in CH_3CN (1.1 mL) was added nitrostyrene (**2b**, 127.3 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 15 h until the completion of the reaction, as monitored by TLC. Then the reaction mixture was directly filtered through a Celite bed (to remove insoluble polymer junk) and washed with EtOAc (15 mL). The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography with 20 % EtOAc–hexane to afford **3b** (39.8 mg, 41% yield) as white solid (R_f = 0.29 in 20% EtOAc–hexane, developed two times on TLC) and **5b** (6.8 mg, 7%) as white solid (R_f = 0.23 in 20% EtOAc-hexane developed two times on TLC).

Select data for **3b**: m.p. 195–196 °C; IR (neat): 3550–3250, 2923, 2852, 1739, 1559, 1514, 1466, 1365, 1316, 1299, 1072, 809, 734 cm^{-1}; ^1H NMR (500 MHz, CD_3CN): δ 7.23 (d, J = 7.5 Hz, 2 H), 7.23 – 7.10 (m, 4 H), 7.08 (d, J = 7.5 Hz, 2 H), 4.92 – 4.87 (m, 1 H), 4.79 (d, J = 12.0 Hz, 1 H), 4.55 – 4.53 (m, 1 H), 4.35 (dd, J = 12.5, 12.5 Hz, 1 H), 4.04 (d, J = 6.5 Hz, 1 H), 2.89 – 2.81 (m, 1 H), 2.80 – 2.70 (m, 1 H), 2.57 (dd, J = 13.0 Hz, 9.0 Hz, 1 H), 2.31 (s, 3 H), 2.20 (s, 3 H), 2.18 – 2.09 (m, 1 H), 0.89 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 214.9 (C), 139.4 (C), 139.0 (C), 133.7 (C), 132.3 (C), 130.2 (4 CH), 130.1 (4 CH), 93.0 (CH), 89.5 (CH), 79.9 (C), 58.2 (C), 49.8 (CH), 41.1 (CH), 34.5 (CH_2), 28.9 (CH_2), 21.13 (CH_3), 21.09 (CH_3), 19.2 (CH_3); MS (*m/z*, relative intensity): 438 (M^+, 2), 349 (9), 326 (5), 279 (9), 219 (73), 163 (32), 129 (33), 115 (100), 105 (83), 91 (79); exact mass calculated for $C_{24}H_{26}N_2O_6$ (M^+): 438.1791; found: 438.1790.

Select data for **5b**: m.p. 164–165 °C; ^1H NMR (500 MHz, CD_3CN): δ 7.33 (d, J = 8.5 Hz, 2 H), 7.16 – 7.11 (m, 6 H), 6.01 (d, J = 12.5 Hz, 1 H), 4.94 (dd, J =4.5 Hz, 4.5Hz, 1 H), 4.30 (dd, J = 13.0 Hz, 4.5 Hz, 1 H), 4.22 (br.s, 1 H), 3.50 (d, J = 4.0 Hz, 1 H), 2.98 – 2.89 (m, 1 H),

2.66 – 2.56 (m, 2 H), 2.33 – 2.24 (m, 1 H), 2.30 (s, 3 H), 2.27 (s, 3 H), 1.0 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 212.7 (C), 139.7 (C), 138.9 (C), 133.5 (C), 133.4 (C), 132.1 (2 CH), 130.8 (2 CH), 129.8 (2 CH), 128.0 (2 CH), 93.6 (CH), 87.7 (CH), 80.4 (C), 55.8 (C), 49.6 (CH), 43.6 (CH), 35.9 (CH_2), 28.8 (CH_2), 21.6 (CH_3), 21.11 (CH_3), 21.09 (CH_3).

Preparation of adduct 3c and 5c.



1 (1 equiv) **2c** (3.5 equiv) **3c** **5c**

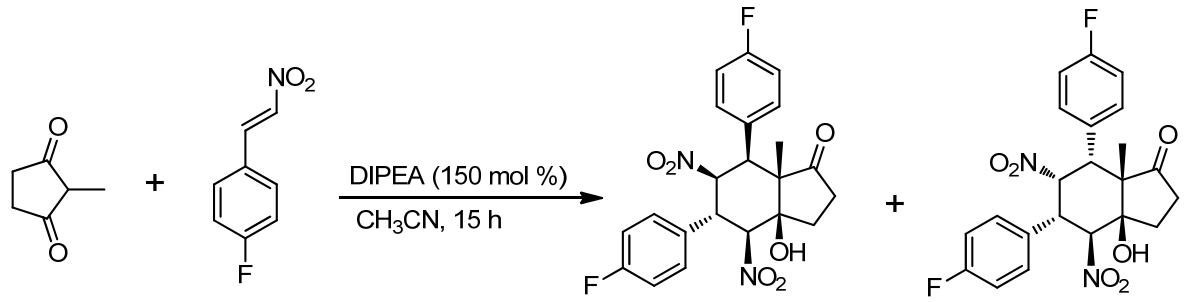
To a solution of DIPEA (44 mg, 0.34 mmol, 1.5 equiv), 2-methyl-1,3-cyclopentanedione (**1**, 25 mg, 0.22 mmol) in CH_3CN (1.1 mL) was added nitrostyrene (**2c**, 139 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 20 h until the completion of the reaction, as monitored by TLC. Then the reaction mixture was directly filtered through a Celite bed (to remove insoluble polymer junk) and washed with EtOAc (15 mL). The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography with 20 % EtOAc–hexane to afford **3c** (21.5 mg, 20% yield) as white solid (R_f = 0.13 in 20% EtOAc–hexane, developed two times on TLC) and **5c** (4.2 mg, 4%) as a pale yellow solid (R_f = 0.09 in 20% EtOAc-hexane developed two times on TLC).

Select data for **3c**: m.p. 196–197 °C; IR (neat): 3550–3250, 2923, 2852, 1740, 1558, 1364, 1299, 1073, 1027, 811, 735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, J = 8.5 Hz, 2 H), 6.87 – 6.80 (m, 4 H), 6.76 (d, J = 8.5 Hz, 2 H), 4.83 (dd, J = 12.0, 7.0 Hz, 1 H), 4.48 (d, J = 12.0 Hz, 1 H), 4.36 (dd, J = 12.5, 12.0 Hz, 1 H), 4.16 (d, J = 6.5 Hz, 1 H), 3.78 (s, 3 H), 3.69 (s, 3 H), 3.46 (s, 1 H), 2.88 (dd, J = 20.0 Hz, 10.5 Hz, 1 H), 2.62 – 2.53 (m, 1 H), 2.31 (dd, J = 13.5 Hz, 9.5 Hz, 1 H), 2.22 – 2.14 (m, 1 H), 0.98 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.8 (C), 159.7 (C), 159.5 (C), 132.5 (2 CH) 125.6 (C), 125.3 (C), 114.5 (2 CH), 114.0 (2 CH), 92.7 (CH), 87.9 (CH), 78.2 (C), 57.2 (C), 55.2 (CH_3), 55.1 (CH_3), 47.5 (CH),

39.9 (CH), 33.9 (CH_2), 28.8 (CH_2), 18.3 (CH_3), some aryl carbons are broadened and disappeared due to the slow rotation and coalescence phenomenon; MS (*m/z*, relative intensity): 470 (M^+, 11), 397 (14), 355 (19), 267 (17), 253 (17), 179 (19), 135 (100), 121 (75), 73 (60); exact mass calculated for $C_{24}H_{26}N_2O_8$ (M^+): 470.1689; found: 470.1689.

Select data for **5c**: mp 103–104 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, J = 9.0 Hz, 2 H), 7.07 (d, J = 8.5 Hz, 2 H), 6.90 – 6.78 (m, 4 H), 6.13 (d, J = 12.5 Hz, 1 H), 4.84 (dd, J =4.5 Hz, 4.0 Hz, 1 H), 4.11 (dd, J =13.0 Hz, 4.5Hz, 1 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 3.36 (s, 1 H), 3.35 (d, J = 16.0 Hz, 1 H), 2.90 – 2.82 (m, 1 H), 2.70 – 2.60 (m, 1 H), 2.36 – 2.30 (m, 1 H), 2.20 – 2.14 (m, 1 H), 1.11 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.8 (C), 160.0 (C), 159.6 (C), 132.0 (2 CH), 128.4 (2 CH), 125.9 (C), 124.8 (C), 114.9 (2 CH), 113.8 (2 CH), 92.4 (CH), 87.1 (CH), 78.8 (C), 55.20 (CH_3), 55.19 (CH_3), 54.6 (C), 49.1(CH), 43.6 (CH), 35.2 (CH_2), 29.0 (CH_2), 20.8 (CH_3).

Preparation of adduct 3d and 5d.



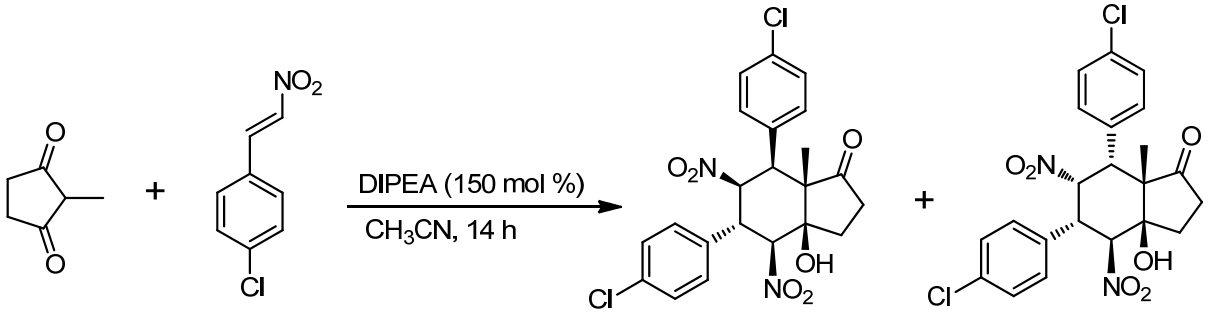
1 (1 equiv) **2d** (3.5 equiv) **3d** **5d**

To a solution of DIPEA (44 mg, 0.34 mmol, 1.5 equiv), 2-methyl-1,3-cyclopentanedione (**1**, 25 mg, 0.22 mmol) in CH_3CN (1.1 mL) was added nitrostyrene (**2d**, 130.2 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 15 h until the completion of the reaction, as monitored by TLC. Then the reaction mixture was directly filtered through a Celite bed (to remove insoluble polymer junk) and washed with EtOAc (15 mL). The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography with 20 % EtOAc–hexane to afford **3d** (59.7 mg, 60% yield) as

white solid (R_f = 0.19 in 20% EtOAc–hexane, developed two times on TLC) and **5d** (7.0 mg, 7% yield) as a pale yellow solid (R_f = 0.13 in 20% EtOAc-hexane developed two times on TLC). Select data for **3d**: m.p. 208–209 °C; IR (neat): 3550–3200, 2922, 2852, 1740, 1606, 1558, 1512, 1364, 1233, 1164, 840, 735 cm^{-1}; ^1H NMR (500 MHz, CD_3CN): δ 7.42 – 7.39 (m, 2 H), 7.18 – 7.03 (m, 4 H), 7.01 (dd, J = 9.0 Hz, 9.0 Hz, 2 H), 4.91 (dd, J = 12.5, 6.5 Hz, 1 H), 4.80 (d, J = 12.0 Hz, 1 H), 4.55 (s, 1 H), 4.38 (dd, J = 12.0, 12.0 Hz, 1 H), 4.12 (d, J = 6.5 Hz, 1 H), 2.90 – 2.82 (m, 1 H), 2.80 – 2.70 (m, 1 H), 2.61 – 2.56 (m, 1 H), 2.20 – 2.11 (m, 1 H), 0.90 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 214.4 (C), 163.7 (d, J = 243.9 Hz, C), 163.4 (d, J = 244.4 Hz, C), 134.5 (2 CH), 132.6 (d, J = 3.4 Hz, C), 131.4 (d, J = 3.4 Hz, C), 116.4 (d, J = 21.6 Hz, 2 CH), 116.2 (d, J = 21.3 Hz, 2 CH), 92.6 (CH), 89.2 (CH), 80.0 (C), 58.1 (C), 49.3 (CH), 40.7 (CH), 34.4 (CH_2), 28.8 (CH_2), 19.1 (CH_3), two aryl carbons and two aryl protons are broadened and disappeared due to the slow rotation and coalescence phenomenon; MS (*m/z*, relative intensity): 446 (M^+, 11), 400 (5), 354 (20), 293 (34), 281 (21), 227 (17), 133 (35), 123 (84), 109 (100); exact mass calculated for $C_{22}H_{20}F_2N_2O_6$ (M^+): 446.1289; found: 446.1287.

Selected data for **5d**: m.p. 170–171 °C; ^1H NMR (500 MHz, CD_3CN): δ 7.53 – 7.49 (m, 2 H), 7.34 – 7.30 (m, 2 H), 7.10 – 7.04 (m, 4 H), 6.00 (d, J =13.0 Hz, 1 H), 4.97 (dd, J = 4.0 Hz, 4.5 Hz, 1 H), 4.38 (dd, J = 13.0 Hz, 4.5 Hz, 1 H), 4.23 (s, 1 H), 3.58 (d, J =4.0 Hz, 1 H), 2.97-2.90 (m, 1 H), 2.70 – 2.59 (m, 2 H), 2.18 – 2.11 (m, 1 H) 1.03 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 212.8 (C), 163.6 (d, J = 244.5 Hz, C), 163.5 (d, J = 243.6 Hz, C), 134.2 (d, J = 8.4 Hz, 2 CH), 132.6 (d, J = 3.4 Hz, C), 132.4 (d, J = 3.3 Hz, C), 130.2 (d, J = 8.4 Hz, 2 CH), 117.1 (d, J = 21.8 Hz, 2 CH), 115.8 (d, J = 21.1 Hz, 2 CH), 93.3 (CH), 87.6 (CH), 80.4 (C), 55.8 (C), 49.1 (CH), 43.2 (CH), 35.8 (CH_2), 28.8 (CH_2), 21.5 (CH_3).

Preparation of adduct 3e and 5e.

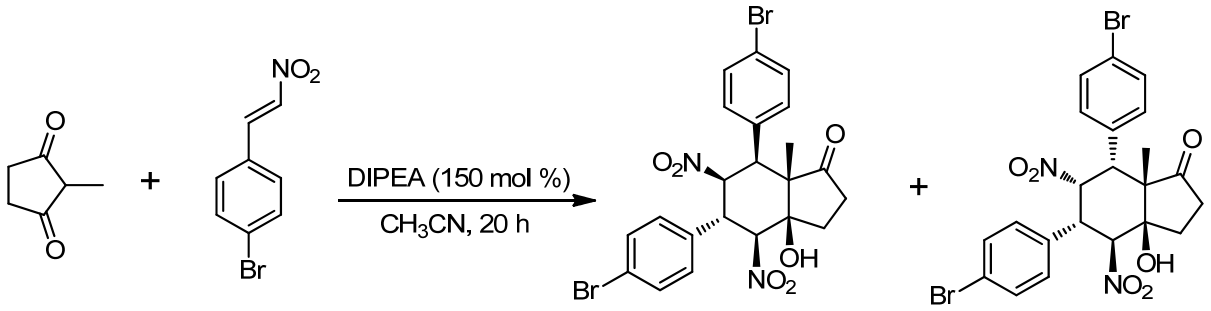


1 (1 equiv) **2e** (3.5 equiv) **3e** **5e**

To a solution of 2-methyl-1,3-cyclopentanedione (**1a,** 25.0 mg, 0.223 mmol, 1.0 equiv) and diisopropylethylamine (43.3 mg, 0.335 mmol, 1.5 equiv) in CH_3CN (1.1 mL) was added nitrostyrene (**2e,** 143.2 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 14 h until the completion of the reaction, as monitored by TLC. Then the reaction mixture was directly filtered through a Celite bed (to remove insoluble polymer junk) and washed with EtOAc (15 mL). The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography with 20 % EtOAc-hexane to afford **3e** (60 mg, 56% yield) as white solid (R_f= 0.21 developed two times in 20 % EtOAc-hexane) and **5e** (7.5 mg, 7% yield) as a pale yellow solid (R_f= 0.16 in 20% EtOAc-hexane developed two times on TLC). Select data for **3e**: m.p. 231–232 ^{o}C; IR (neat): 3491, 2922, 2851, 1740, 1558, 1493, 1468, 1415, 1362, 1095, 836, 739 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN): δ 7.41 – 7.38 (m, 4H), 7.27 (d, J = 6.5 Hz, 4H), 4.92 (dd, J = 12.5 Hz, 6.5 Hz, 1H), 4.80 (d, J = 12.0 Hz, 1H), 4.58 (s, 1H), 4.36 (dd, J = 12.5 Hz, 12.0 Hz, 1H), 4.11 (d, J = 6.5 Hz, 1H), 2.90 – 2.84 (m, 1H), 2.79 – 2.71 (m, 1H), 2.61 – 2.57 (m, 1H), 2.14 – 2.11 (m, 1H),0.90 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN): δ 214.3 (C), 135.4 (C), 134.9 (C), 134.8 (C), 134.1 (C), 129.7 (4 CH), 129.6 (4 CH), 92.4 (CH), 89.0 (CH), 79.9 (C), 58.0 (C), 49.4 (CH), 40.9 (CH), 34.4 (CH_2), 28.7 (CH_2), 19.1 (CH_3); exact mass calculated for $C_{22}H_{20}Cl_2N_2O_6$ (M^+): 478.0698; found: 478.0696.

Selected data for **5e**: m.p. 137–138 °C; ^{1}H NMR (500 MHz, CD_3CN): δ 7.49 (dd, J =11.5 Hz, 3.0 Hz, 2 H), 7.36 – 7.32 (m, 4 H), 7.30 – 7.27 (m, 2 H), 5.99 (d, J =12.5 Hz, 1 H), 4.97 (dd, J = 4.5 Hz, 4.0 Hz, 1 H), 4.38 (dd, J = 13.0 Hz, 4.5 Hz, 1 H), 4.32 (s, 1 H), 3.58 (d, J =4.0 Hz, 1 H), 3.00 – 2.90 (m, 1 H), 2.70 – 2.59 (m, 2 H), 2.11-2.07 (m, 1 H), 1.03 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 212.7 (C), 135.3 (C), 135.2 (C), 135.1 (C), 134.7 (C), 133.9 (2 CH), 130.3 (2 CH), 129.8 (2 CH), 129.2 (2 CH), 92.9 (CH), 87.3 (CH), 80.4 (C), 55.8 (C), 49.2 (CH), 43.3 (CH), 35.8 (CH_2), 28.7 (CH_2), 21.5 (CH_3).

Preparation of adduct 3f and 5f.



1 (1 equiv) **2f** (3.5 equiv) **3f** **5f**

To a solution of DIPEA (44 mg, 0.34 mmol, 1.5 equiv), 2-methyl-1,3-cyclopentanedione (**1**, 25 mg, 0.22 mmol) in CH_3CN (1.1 mL) was added nitrostyrene (**2f**, 178 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 20 h until the completion of the reaction, as monitored by TLC. Then the reaction mixture was directly filtered through a Celite bed (to remove insoluble polymer junk) and washed with EtOAc (15 mL). The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography with 20 % EtOAc–hexane to afford **3f** (57.8 mg, 46% yield) as white solid (R_f = 0.20 in 20% EtOAc–hexane, developed two times on TLC) and **5f** (12.7 mg, 10% yield) as a pale yellow solid (R_f = 0.15 in 20% EtOAc-hexane developed two times on TLC). Select data for **3f**: m.p. 232–233 °C; IR (neat): 3600–3400, 2922, 2852, 1740, 1558, 1487, 1362, 1068, 1013, 828, 736 cm^{-1}; ^1H NMR (500 MHz, $CS_2/CDCl_3$): δ 7.47 – 7.41 (m, 4 H), 7.39 (d, J = 8.5 Hz, 2 H), 7.05 (d, J = 8.5 Hz, 2 H), 4.82 (dd, J = 12.0, 6.5 Hz, 1 H), 4.46 (d, J = 12.5 Hz, 1 H), 4.35 (dd, J = 12.5, 12.5 Hz, 1 H), 4.17 (d, J = 7.0 Hz, 1 H), 3.46 (s, 1 H), 2.95 – 2.88 (m, 1 H), 2.64 – 2.53 (m, 1 H), 2.40 – 2.31 (m, 1 H), 2.23 – 2.15 (m, 1 H), 0.98 (s, 3 H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$): δ 211.8 (C), 132.5 (C), 132.3 (4 CH), 132.1 (C), 131.9 (4 CH), 123.3 (C), 123.1 (C), 91.9 (CH), 87.2 (CH), 78.1 (C), 56.8 (C), 47.5 (CH), 40.0 (CH), 33.7 (CH_2), 28.5 (CH_2), 18.1 (CH_3); IR (neat): 3725, 3705, 3654, 3634, 2922, 2852, 1740, 1558, 1487, 1362, 1299, 1170, 1068, 1013, 828, 736 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.45 (m, 4 H), 7.39 (d, J = 8.5 Hz, 2 H), 7.06 (d, J = 8.5 Hz, 2 H), 4.82 (dd, J = 5.0, 7.0 Hz, 1 H), 4.46 (d, J = 12.0 Hz, 1 H), 4.35 (dd, J = 12.5, 12.5 Hz, 1 H), 4.18 (d, J = 7.0 Hz, 1 H), 3.50 (s, 1 H), 2.94 – 2.86 (m, 1 H), 2.63 – 2.55 (m, 1 H), 2.39 – 2.34 (m, 1 H), 2.22 – 2.16 (m, 1 H), 0.98 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.1 (C), 132.7 (C), 132.4 (C), 132.2 (4 CH), 132.0 (4 CH), 123.2 (C), 123.1 (C), 92.0 (CH), 87.3 (CH), 78.2 (C), 56.9 (C), 47.6 (CH), 40.1 (CH), 33.8 (CH_2), 28.5 (CH_2), 18.2 (CH_3); MS (m/*z*, relative intensity): 570 (M^++4, 20), 568 (M^++2, 40), 566 (M^+, 20), 476 (51), 415 (39), 403 (28), 349 (34), 284 (32), 202 (57), 169 (72), 102 (100); exact mass calculated for $C_{22}H_{20}Br_2N_2O_6$ (M^+): 565.9688; found: 565.9688.

Select data for **5f**: m.p. 151–152 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 4 H), 7.29 (d, J = 8.0 Hz, 2 H), 7.04 (d, J = 8.0 Hz, 2 H), 6.10 (d, J = 13.0 Hz, 1 H), 4.83 (dd, J =4.5 Hz, 4.0 Hz, 1 H), 4.15 (dd, J =12.5 Hz, 4.5 Hz, 1 H), 3.39 (d, J = 4.0 Hz, 1 H), 3.30 (s, 1 H), 2.90 – 2.83 (m, 1 H), 2.72 – 2.66 (m, 1 H), 2.41 – 2.35 (m, 1 H), 2.20 – 2.15 (m, 1 H), 1.11 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.3 (C), 132.8 (2 CH), 132.7 (C), 132.5 (2 CH), 131.8 (2 CH), 128.8 (2 CH), 123.7 (C), 123.0 (C), 91.3 (CH), 86.5 (CH), 78.8 (C), 54.4 (C), 49.3 (CH), 43.7 (CH), 35.0 (CH_2), 30.9 (C), 28.8 (CH_2), 20.7 (CH_3).

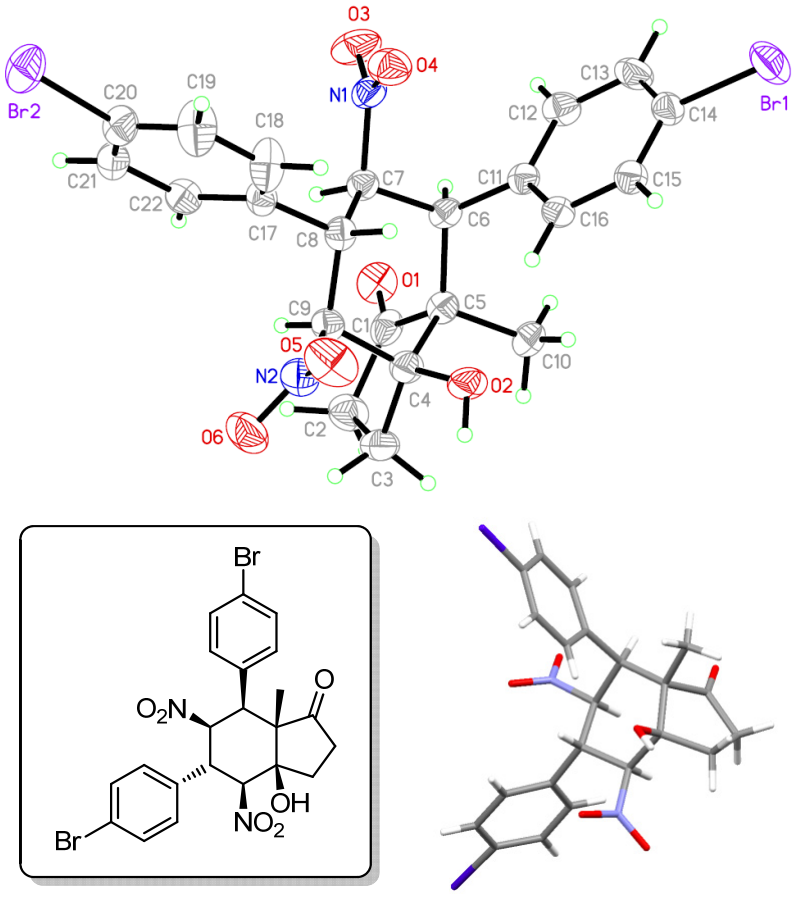


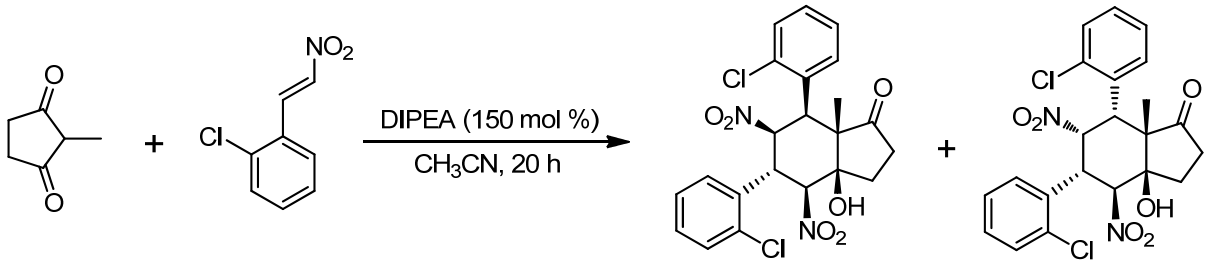
Figure S3. ORTEP and Stereo plots for X-ray crystal structures of (±)-**3f**.

CCDC 1474865 contains the supplementary crystallographic data for (±)-**3f**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Crystal data and structure refinement for (±)-**3f**.

Identification code	ic17312	
Empirical formula	$C_{25}H_{26}Br_2N_2O_7$	
Formula weight	626.30	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4202(7) Å	a= 61.4060(13)°.
	b = 12.1455(8) Å	b= 71.1351(14)°.
	c = 12.5464(8) Å	g = 78.7175(14)°.
Volume	1317.70(15) $Å^3$	
Z	2	
Density (calculated)	1.578 Mg/m^3	
Absorption coefficient	3.122 mm^{-1}	
F(000)	632	
Crystal size	0.250 x 0.200 x 0.120 mm^3	
Theta range for data collection	1.912 to 27.498°.	
Index ranges	-13<=h<=13, -15<=k<=15, -16<=l<=16	
Reflections collected	17236	
Independent reflections	6063 [R(int) = 0.0345]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.706 and 0.509	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6063 / 114 / 340	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.0929	
R indices (all data)	R1 = 0.0579, wR2 = 0.0998	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.760 and -0.440 $e.Å^{-3}$	

Preparation of Compound 3g and 5g:



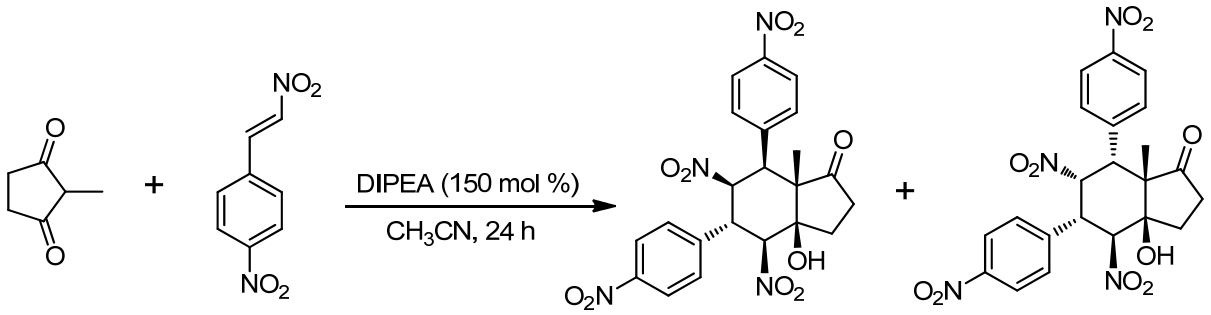
1 (1 equiv) **2g** (3.5 equiv) **3g** **5g**

To a solution of 2-methyl-1,3-cyclopentanedione (**1,** 25.0 mg, 0.223 mmol, 1.0 equiv) and diisopropylethylamine (43.3 mg, 0.335 mmol, 1.5 equiv) in CH_3CN (1.1 mL) was added nitrostyrene (**2g,** 143.2 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 20 h until the completion of the reaction, as monitored by TLC. The solution was diluted with EtOAc (10 mL), washed with water (5 mL) and brine (5 mL), dried over $MgSO_4$ and concentrated in *vacuo* to give the crude residue. The crude product was purified by flash column chromatography with 25 % EtOAc–hexane (R_f = 0.21 for **3g** in 20 % EtOAc–hexane developed two times on TLC) to afford **3g** (86.6 mg, 81% yield) as white solid (R_f = 0.21 for **3g** in 20 % EtOAc–hexane developed two times on TLC) and **5g** (11.8 mg, 11% yield) as white solid (R_f = 0.26 in 20% EtOAc-hexane developed two times on TLC); Select data for **3g**: m.p. 212–213 °C; IR (neat): 3550–3250, 3069, 3015, 2988, 2961, 1733, 1559, 1477, 1445, 1365, 1321, 1173, 1112, 1089, 1037, 980, 908, 811, 759 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6): δ 8.67 (d, J = 8.0 Hz, 1 H), 7.89 – 7.86 (m, 1 H), 7.48 (dd, J = 8.0, 7.0 Hz, 1 H), 7.43 (d, J = 7.0 Hz, 1 H), 7.37 – 7.33 (m, 2 H), 7.26 – 7.22 (m, 2 H), 5.92 (s, 1 H), 5.42 (dd, J = 12.0, 12.0 Hz, 1 H), 5.33 (d, J = 6.5 Hz, 1 H), 5.28 (d, J = 12.0 Hz, 1 H), 5.19 (dd, J = 12.5 Hz, 6.5 Hz, 1 H), 2.92 – 2.86 (m, 2 H), 2.78 – 2.70 (m, 1 H), 2.32 (dd, J = 10.5 Hz, 3.0 Hz, 1 H), 0.94 (s, 3 H); ^{13}C NMR (125 MHz, acetone-d_6): δ 214.0 (C), 137.7 (C), 137.2 (C), 134.8 (C), 134.5 (CH), 133.2 (C), 131.1 (CH), 130.8 (CH), 130.5 (CH), 130.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 92.4 (CH), 88.8 (CH), 80.2 (C), 58.4 (C), 43.6 (CH), 37.0 (CH), 34.0 (CH_2), 28.7 (CH_2), 18.8 (CH_3); MS (*m/z*, relative intensity): 480 (M^++2, 13), 478 (M^+, 20), 443 (36), 367 (48), 325 (100), 202 (30), 165 (27), 139 (36), 125 (82); exact mass calculated for $C_{22}H_{20}Cl_2N_2O_6$ (M^+): 478.0698; found: 478.0703.

Select data for **5g**: m.p. 99–100°C; ^1H NMR (500 MHz, acetone-d_6): δ 8.38 (dd, J = 8.0

Hz, 1.5Hz, 1 H), 7.56 (d, J = 8.0 Hz, 1 H), 7.50 – 7.40 (m, 3 H), 7.35 – 7.28 (m, 3 H), 6.30 (d, J = 12.0 Hz, 1 H), 5.91 (s, 1 H), 5.02 – 4.98 (m, 2 H), 4.91 (d, J = 2.5 Hz, 1 H), 3.12 – 3.08 (m, 1 H), 2.98 – 2.93 (m, 1 H), 2.84 – 2.79 (m, 1 H), 2.51 – 2.48 (m, 1 H), 1.07 (s, 3 H); ^{13}C NMR (125 MHz, acetone-d_6): δ 213.5 (C), 135.73 (C), 135.68 (C), 134.9 (C), 133.9 (C), 132.4 (CH), 131.2 (CH), 131.1 (CH), 130.9 (CH), 130.6 (CH), 128.8 (CH), 128.4 (CH), 127.6 (CH), 89.9 (CH), 87.5 (CH), 80.1 (C), 56.5 (C), 43.4 (CH), 37.1 (CH), 34.8 (CH_2), 31.0 (CH_2), 18.9 (CH_3).

Preparation of adduct 3h and 5h.



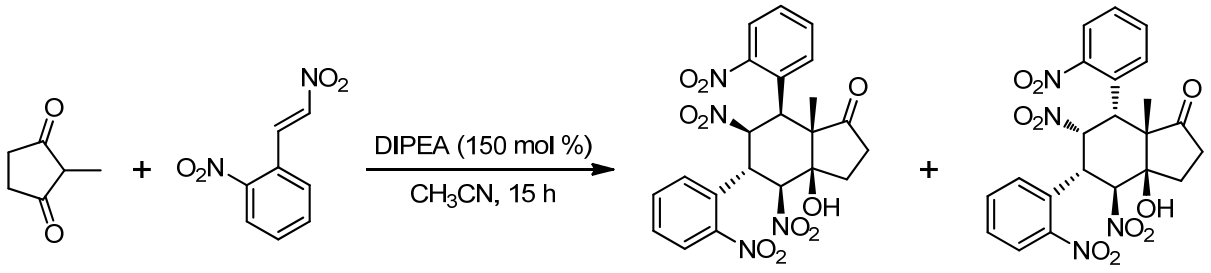
1 (1 equiv) **2h** (3.5 equiv) **3h** **5h**

To a solution of DIPEA (44 mg, 0.34 mmol, 1.5 equiv), 2-methyl-1,3-cyclopentanedione (**1**, 25 mg, 0.22 mmol) in CH_3CN (1.1 mL) was added nitrostyrene (**2h**, 151.4 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 24 h until the completion of the reaction, as monitored by TLC. Then the reaction mixture was directly filtered through a Celite bed (to remove insoluble polymer junk) and washed with EtOAc (15 mL). The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography with 30% EtOAc–hexane to afford **3h** (85.9 mg, 77% yield) as white solid (R_f = 0.22 in 30% EtOAc–hexane developed two times on TLC) and **5h** (19.0 mg, 17% yield) as pale yellow solid (R_f = 0.17 in 30% EtOAc-hexane developed two times on TLC). Select data for **3h**: m.p. 194 °C (decompose). IR (neat): 3550–3300, 3118, 3082, 2922, 2856, 1743, 1604, 1559, 1522, 1350, 1110, 1068, 858, 734 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN): δ

8.40 – 8.30 (m, 4 H), 8.27 (d, J = 8.5 Hz, 2 H), 7.82 (d, J = 8.5 Hz, 2 H), 5.22 (dd, J = 12.5 Hz, 6.5 Hz, 1H), 5.08 (d, J = 12.0 Hz, 1 H), 4.98 (d, J = 7.5 Hz, 1 H), 4.73 (dd, J = 12.0, 12.5 Hz, 1 H), 4.47 (d, J = 6.5 Hz, 1 H), 3.07 (dd, J = 20.5 Hz, 9.0 Hz, 1 H), 3.00 – 2.90 (m, 1 H), 2.83 – 2.78 (m, 1 H), 1.08 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 213.7 (C), 149.1 (C), 143.7 (C), 142.5 (C), 133.9 (C), 124.7 (4 CH), 124.5 (4 CH), 92.0 (CH), 88.6 (CH), 80.0 (C), 57.9 (C), 49.5 (CH), 41.4 (CH), 34.4 (CH_2), 28.5 (CH_2), 19.0 (CH_3); MS (*m/z*, relative intensity): 500 (M^+, 1), 134 (59), 104 (87), 92 (81), 89 (55), 77 (100), 76 (71); exact mass calculated for $C_{22}H_{20}N_4O_{10}$ (M^+): 500.1179; found: 500.1182.

Selected data for **5h**: mp. 150–151 °C; ^{1}H NMR (500 MHz, CD_3CN): δ 8.17 (d, J = 8.5 Hz, 2 H), 8.16 (J = 8.5 Hz, 2 H), 7.78 (d, J = 8.5 Hz, 2 H), 7.57 (d, J = 8.5 Hz, 2 H), 6.09 (d, J = 12.5 Hz, 1 H), 5.08 (dd, J = 4.5 Hz, 4.0 Hz, 1 H), 4.59 (dd, J = 12.5 Hz, 4.5 Hz, 1 H), 3.80 (d, J = 4.0 Hz, 1 H), 3.02 – 2.95 (m, 1 H), 2.78 (dd, J = 13.5 Hz, 9.0 Hz, 1 H), 2.67 (dd, J = 20.0 Hz, 9.0 Hz, 1 H), 2.23 – 2.08 (m. 1 H), 1.06 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 212.7 (C), 149.2 (C), 148.9 (C), 143.5 (2 C), 133.5 (2 CH), 129.5 (2 CH), 125.3 (2 CH), 124.1 (2 CH), 91.9 (CH), 87.1 (CH), 80.5 (C), 55.9 (C), 49.4 (CH), 43.7 (CH), 35.7 (CH_2), 28.6 (CH_2), 21.4 (CH_3).

Preparation of Compound 3i and 5i:



1 (1 equiv) **2i** (3.5 equiv) **3i** **5i**

To a solution of DIPEA (44 mg, 0.34 mmol, 1.5 equiv), 2-methyl-1,3-cyclopentanedione (**1**, 25 mg, 0.22 mmol) in CH_3CN (1.1 mL) was added nitrostyrene (**2i**, 151.4 mg, 0.78 mmol, 3.5 equiv) and the resulting solution was stirred at room temperature for 15 h until the completion of the reaction, as monitored by TLC. The solution was diluted with EtOAc (10

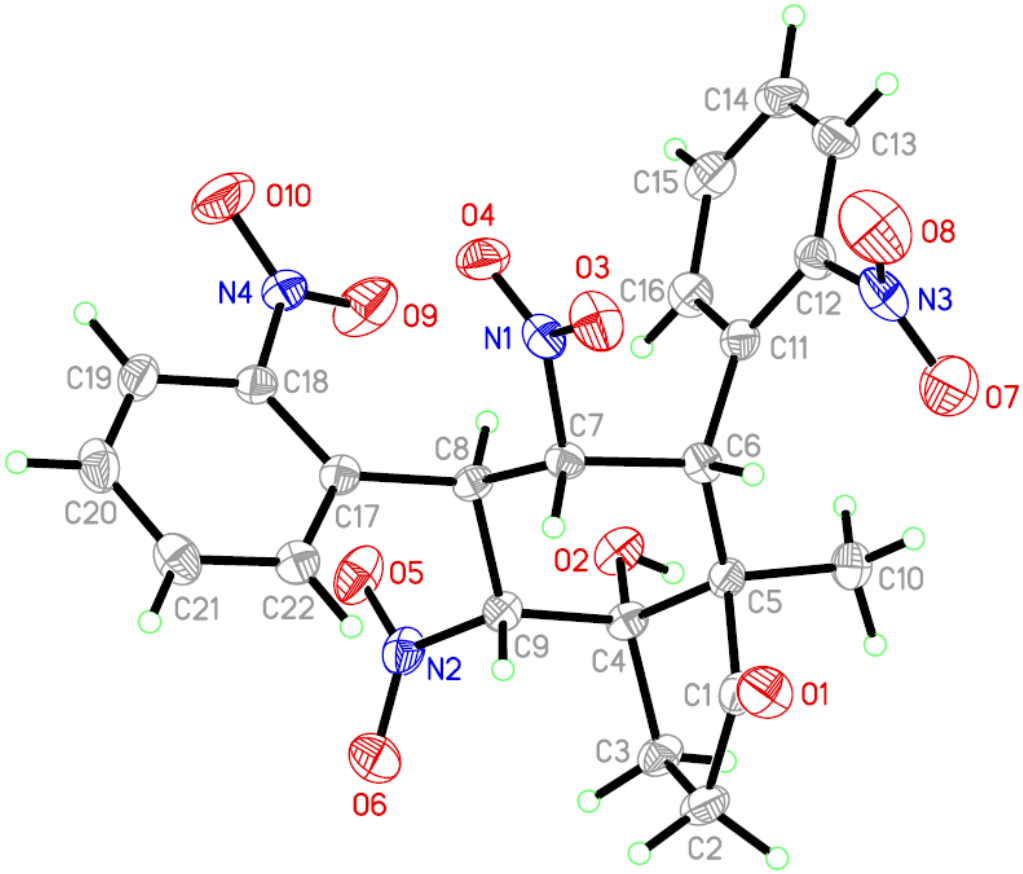
mL), washed with water (5 mL) and brine (5 mL), dried over $MgSO_4$ and concentrated in *vacuo* to give the crude residue. The crude product was purified by flash column chromatography with 20% to 30 % EtOAc–hexane (R_f = 0.14 for **5i**, R_f = 0.07 for **3i**, in 20% EtOAc–hexane developed twice on TLC) to afford **5i** as pale yellow solid (33 mg, 30% yield) and **3i** as pale yellow solid (42 mg, 38% yield).

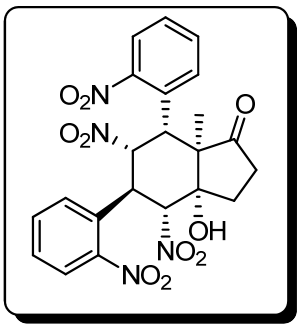
Selected data for **3i**: m.p. 184 °C (decomposed). IR (neat): 3550–3200, 2924, 2854, 1743, 1561, 1529, 1449, 1351, 1073, 855, 787, 735 cm^{-1}; ^1H NMR (500 MHz, CD_3CN): δ 8.62 (d, J = 7.0 Hz, 1 H), 7.90 (d, J = 8.5 Hz, 1 H), 7.83 (dd, J = 8.0 Hz, 8.0 Hz, 1 H), 7.74 – 7.70 (m, 2 H), 7.64 – 7.56 (m, 2 H), 7.47 (dd, J = 8.5 Hz, 7.0 Hz, 1 H), 5.83 (dd, J = 12.0, 11.5 Hz, 1 H), 4.98 (dd, J = 11.5, 6.5 Hz, 1 H), 4.95 (d, J = 6.5 Hz, 1 H), 4.92 (brs, 1 OH), 4.89 (d, J = 12.0 Hz, 1 H), 2.91 – 2.88 (m, 1 H), 2.80 – 2.76 (m, 1 H), 2.64 – 2.60 (m, 1 H), 2.19 – 2.17 (m, 1 H), 1.00 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 213.7 (C), 153.7 (C), 151.7 (C), 134.84 (CH), 134.77 (CH), 133.3 (CH), 130.9 (CH), 130.8 (CH), 130.7 (C), 128.4 (CH), 127.7 (C), 127.1 (CH), 125.5 (CH), 92.3 (CH), 88.6 (CH), 80.3 (C), 58.3 (C), 42.3 (CH), 34.3 (CH), 34.2 (CH_2), 28.3 (CH_2), 18.5 (CH_3); ^1H NMR (500 MHz, acetone-d_6): δ 8.81 (d, J =8.0 Hz, 1 H), 8.08 (d, J = 8.0 Hz, 1 H), 7.98 (d, J = 7.0 Hz, 1 H), 7.85 (dd, J = 8.0, 1.5 Hz, 1 H), 7.76 (dd, J =8.0 Hz, 1.5 Hz, 1 H), 7.67 – 7.62 (m, 2 H), 7.55 – 7.51 (m, 1 H), 6.15 (s, 1 H), 6.07 (dd, J =12.0 Hz, 12.0 Hz, 1 H), 5.36 (d, J = 12.0 Hz, 1 H), 5.26 (dd, J = 12.5, 6.5 Hz, 1 H), 5.04 (d, J = 6.5 Hz, 1 H), 2.96 – 2.92 (m, 1 H), 2.88 – 2.72 (m, 2 H), 2.40 – 2.32 (m, 1 H), 1.09 (s, 3H); ^{13}C NMR (125 MHz, acetone-d_6): δ 213.2 (C), 153.9 (C), 151.7 (C), 134.9 (CH), 134.6 (CH), 132.9 (CH), 131.5 (C), 130.6 (CH), 130.4 (CH), 128.4 (CH), 128.0 (C), 126.9 (CH), 125.2 (CH), 92.5 (CH), 88.7 (CH), 80.3 (C), 58.2 (C), 42.3 (CH), 34.4 (CH), 33.9 (CH_2), 28.5 (CH_2), 18.5 (CH_3); exact mass calculated for $C_{22}H_{20}N_4O_{10}$ (M^+): 500.1179; found: 500.1182.

Selected data for **5i**: m.p 186–187 °C. IR (neat): 3550–3250, 2951, 2923, 2852, 1745, 1556, 1525, 1459, 1348, 1296, 857, 789, 739 cm^{-1}; ^1H NMR (500 MHz, CD_3CN): δ 8.17 (d, J = 8.0 Hz, 1 H), 7.99 (d, J = 8.0 Hz, 1 H), 7.91 (d, J = 8.0 Hz, 1 H), 7.79 (dd, J = 8.0 Hz, 6.0 Hz, 1 H), 7.64 – 7.60 (m, 2 H), 7.56 – 7.52 (m, 1 H), 7.36 (d, J = 8.0 Hz, 1 H), 6.04 (d, J = 12.5 Hz, 1 H), 5.54 (dd, J = 6.0 Hz, 5.5 Hz, 1 H), 4.99 (dd, J = 12.5 Hz, 6.0 Hz, 1 H), 4.56 (d, J = 5.5 Hz, 1 H), 2.95 – 2.90 (m, 1 H), 2.85 – 2.77 (m, 1 H), 2.75 – 2.68 (m, 1 H), 2.42 – 2.36 (m, 1 H), 1.03 (s, 3 H); ^{13}C NMR (125 MHz, CD_3CN): δ 214.5 (C), 151.4 (C), 150.9 (C),

135.3 (CH), 134.2 (CH), 132.6 (CH), 131.1 (CH), 130.9 (CH), 130.7 (C), 130.6 (C), 127.9 (CH), 127.0 (CH), 126.1 (CH), 90.7 (CH), 88.8 (CH), 80.7 (C), 56.6 (C), 41.5 (CH), 36.4 (CH), 35.3 (CH_2), 31.6 (CH_2), 18.3 (CH_3).

A sample of 15 mg of racemic **3i,** prepared as described above, was dissolved with CH_2Cl_2 (15 mL) in a vial, followed by the slow addition of hexane (2 mL) down the inside of the vial and the two-layer solution was maintained throughout the addition process. The solution was capped and left to stand at room temperature for slow evaporation over 5 days to give some crystals (ca. 100 crystals) of the compound **3i**. A crystal was subjected for the single crystal X-ray analysis (crystal ID: ic17971, as shown in the **Figure S4** and **Table S4**). Surprisingly, a chiral space group: orthorhombic $P2_12_12_1$ was observed in the crystal! In order to understand the sign of its specific rotation and to probe the approximate frequency of occurrence of the SDE effect in the recrystallization process, another two crystals from the same batch were arbitrarily selected and subjected for single crystal X-ray analysis. Notably, each of them had the same chiral space group, orthorhombic $P2_12_12_1$, with the same absolute configuration as the previous crystal. The two single crystal X-ray analyses are shown in the **Figure S5**, **Table S5** (for crystal ID: ic18028), **Figure S6**, and **Table S6** (for crystal ID: ic18028_1). On the other hand, another batch of ca. 40 mg of racemic **3i** was subject to the same recrystallization process as described previously to give ca. 150 crystals. From them, 46 crystals were arbitrarily selected and individually subjected to the HPLC analysis with a chiral column (Chiralpack IC). Eluent: 25% THF–hexane, flow rate: 1.0 mL/min. The two enantiomers were separated at R_t 5.6 min and R_t 8.0 min. For the 46 crystals analyzed, 16 of them eluted with R_t 5.6 min (>99% *ee*), 14 of them eluted with R_t 8.0 min (>99% *ee*), 2 of them displayed >80% *ee*, 4 of them were almost a racemate, and 10 of them had low *ee*. The pure enantiomer was individually collected, checking with the aid of the HPLC analysis, and subjected to optical rotation analysis. For R_t 5.6 min: $[\alpha]_D^{29}$ +10.2 (*c* 0.58, acetone); for R_t 8.0 min: $[\alpha]_D^{29}$ –9.1 (*c* 0.36, acetone). Moreover, the above two crystals investigated by X-ray (CCDC 1488798 and CCDC 1488808) were individually subjected to HPLC analysis, comparing and co-injecting with the previous samples, with the conclusion that the chiral X-ray structures obtained herein are (–)-**3i**.





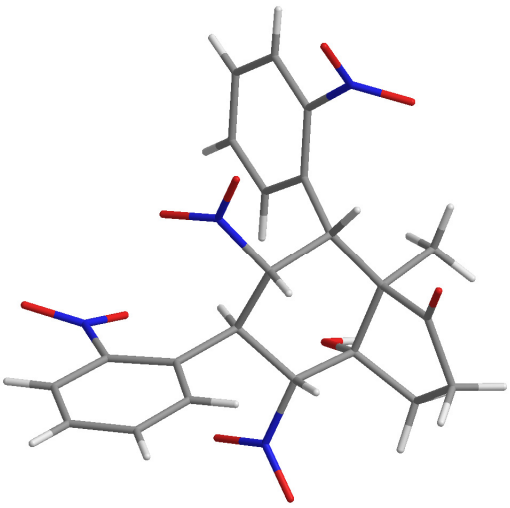
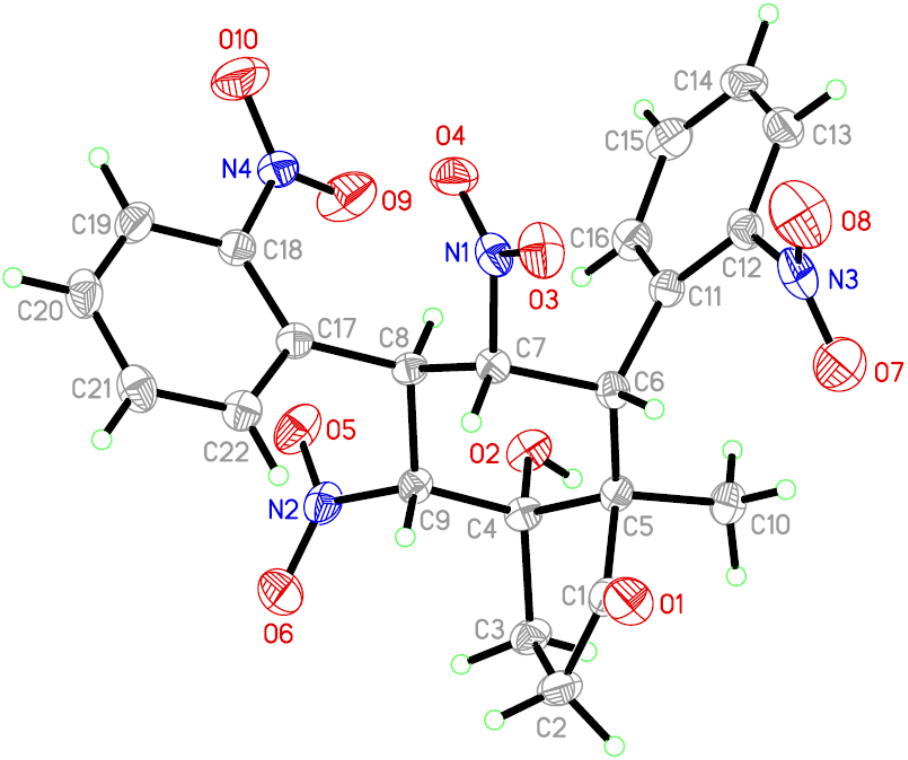


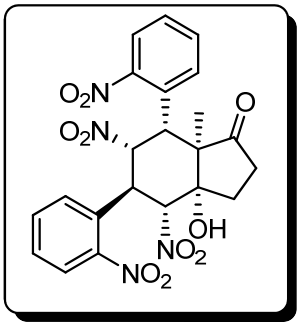
Figure S4. ORTEP, thermal ellipsoids drawn at the 50% probability level, and stereo plots for X-ray crystal structures of (–)-**3i**.

CCDC 1485986 contain the supplementary crystallographic data for this crystal. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S4. Crystal data and structure refinement for (–)-**3i,** first crystal (CCDC 1485986).

Identification code	ic17971	
Empirical formula	C22 H20 N4 O10	
Formula weight	500.42	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.3887(2) Å	α= 90°.
	b = 11.6113(3) Å	β= 90°.
	c = 19.7433(5) Å	γ = 90°.
Volume	2152.32(9) $Å^3$	
Z	4	
Density (calculated)	1.544 Mg/m^3	
Absorption coefficient	1.064 mm^{-1}	
F(000)	1040	
Crystal size	0.222 x 0.182 x 0.166 mm^3	
Theta range for data collection	4.417 to 69.904°.	
Index ranges	-11<=h<=11, -14<=k<=14, -18<=l<=23	
Reflections collected	10046	
Independent reflections	4021 [R(int) = 0.0168]	
Completeness to theta = 67.679°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6531	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4021 / 0 / 328	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0698	
R indices (all data)	R1 = 0.0258, wR2 = 0.0701	
Absolute structure parameter	0.06(3)	
Extinction coefficient	0.0039(3)	
Largest diff. peak and hole	0.227 and -0.158 e.$Å^{-3}$	





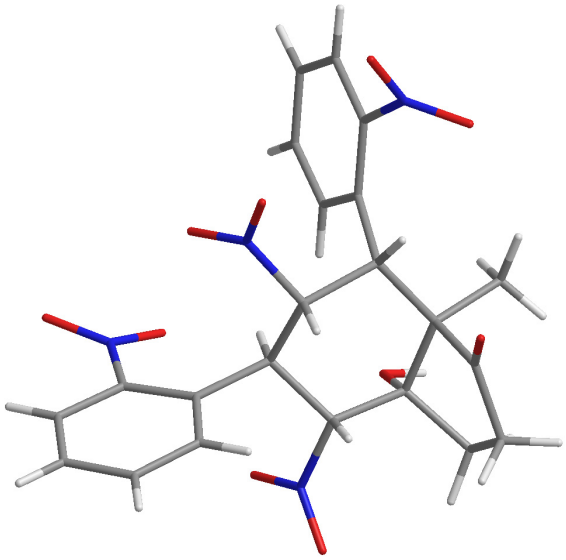


Figure S5. ORTEP, thermal ellipsoids drawn at the 50% probability level, and stereo plots for X-ray crystal structures of (–)-**3i**.

CCDC 1488798 contain the supplementary crystallographic data of this crystal data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S5. Crystal data and structure refinement for (–)-**3i,** second crystal (CCDC 1488798).

Identification code	ic18028	
Empirical formula	C22 H20 N4 O10	
Formula weight	500.42	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.3839(2) Å	α= 90°.
	b = 11.6090(2) Å	β= 90°.
	c = 19.7514(4) Å	γ = 90°.
Volume	2151.67(7) $Å^3$	
Z	4	
Density (calculated)	1.545 Mg/m^3	
Absorption coefficient	1.064 mm^{-1}	
F(000)	1040	
Crystal size	0.333 x 0.298 x 0.157 mm^3	
Theta range for data collection	4.418 to 69.962°.	
Index ranges	-10<=h<=11, -14<=k<=12, -24<=l<=23	
Reflections collected	12358	
Independent reflections	4066 [R(int) = 0.0174]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6145	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4066 / 0 / 328	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0240, wR2 = 0.0617	
R indices (all data)	R1 = 0.0245, wR2 = 0.0621	
Absolute structure parameter	-0.01(3)	
Extinction coefficient	0.0047(3)	
Largest diff. peak and hole	0.224 and -0.128 $e.Å^{-3}$	

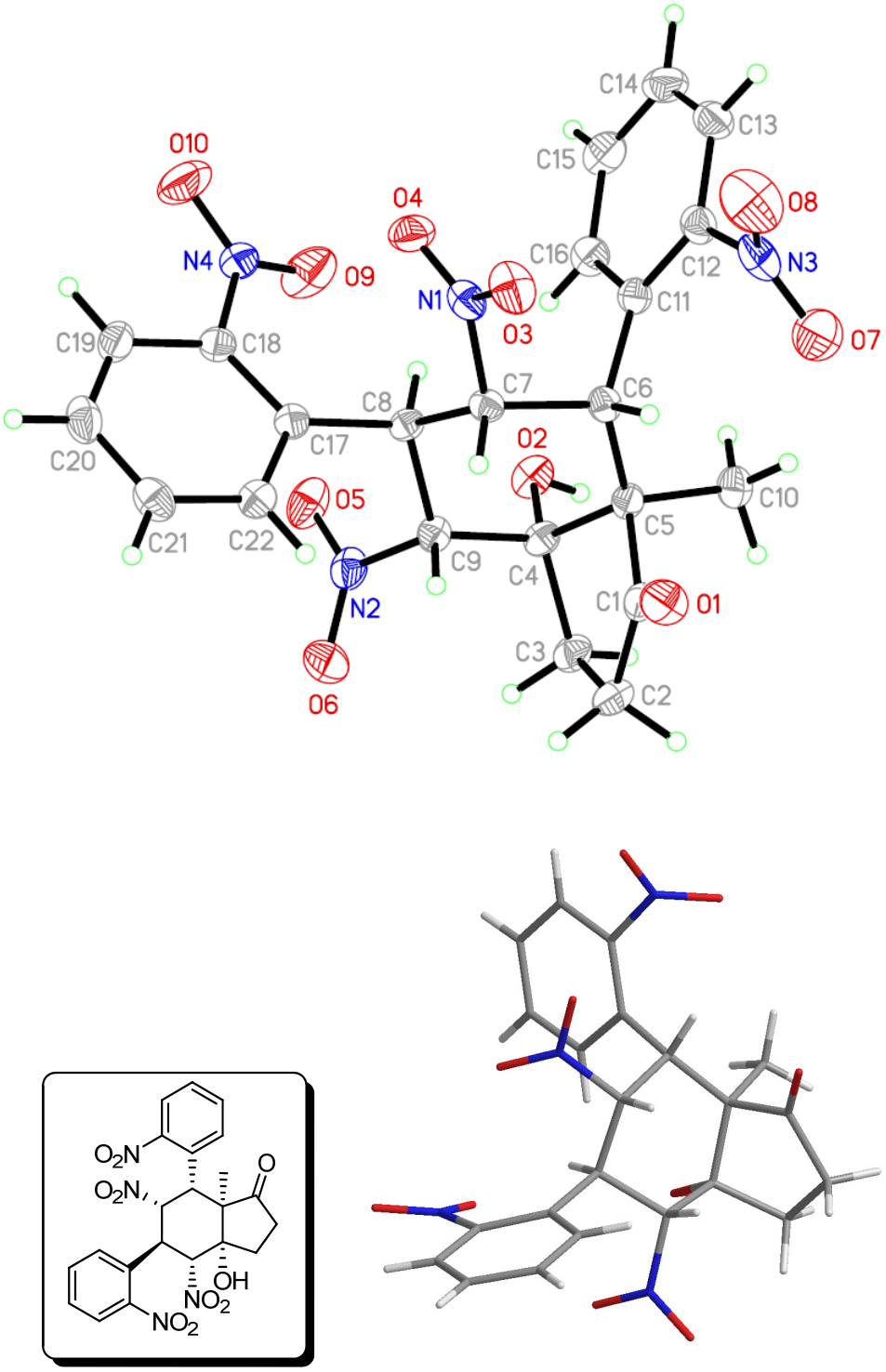


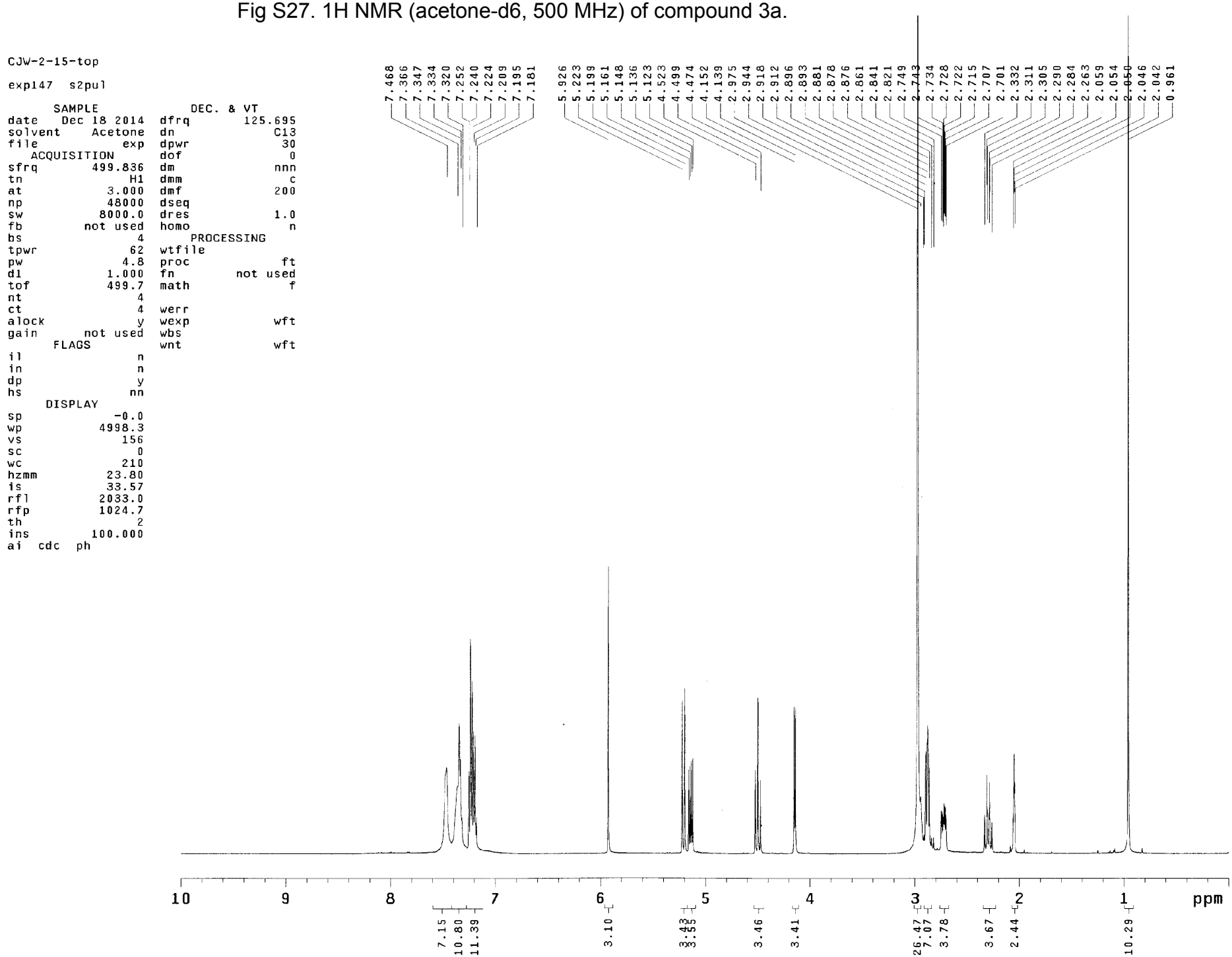
Figure S6. ORTEP, thermal ellipsoids drawn at the 50% probability level, and stereo plots for X-ray crystal structures of (–)-**3i**.

CCDC 1488808 contain the supplementary crystallographic data of this crystal. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S6. Crystal data and structure refinement for (–)-**3i,** third crystal (CCDC 1488808).

Identification code	ic18028_1	
Empirical formula	C22 H20 N4 O10	
Formula weight	500.42	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.38810(10) Å	α= 90°.
	b = 11.6070(2) Å	β= 90°.
	c = 19.7468(3) Å	γ = 90°.
Volume	2151.76(5) $Å^3$	
Z	4	
Density (calculated)	1.545 Mg/m^3	
Absorption coefficient	1.064 mm^{-1}	
F(000)	1040	
Crystal size	0.333 x 0.298 x 0.157 mm^3	
Theta range for data collection	4.418 to 69.931°.	
Index ranges	-11<=h<=10, -13<=k<=14, -24<=l<=23	
Reflections collected	10354	
Independent reflections	4066 [R(int) = 0.0181]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5782	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4066 / 0 / 328	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0247, wR2 = 0.0629	
R indices (all data)	R1 = 0.0253, wR2 = 0.0634	
Absolute structure parameter	-0.06(4)	
Extinction coefficient	0.0034(3)	
Largest diff. peak and hole	0.213 and -0.144 $e.Å^{-3}$	

Fig S27. 1H NMR (acetone-d6, 500 MHz) of compound 3a.



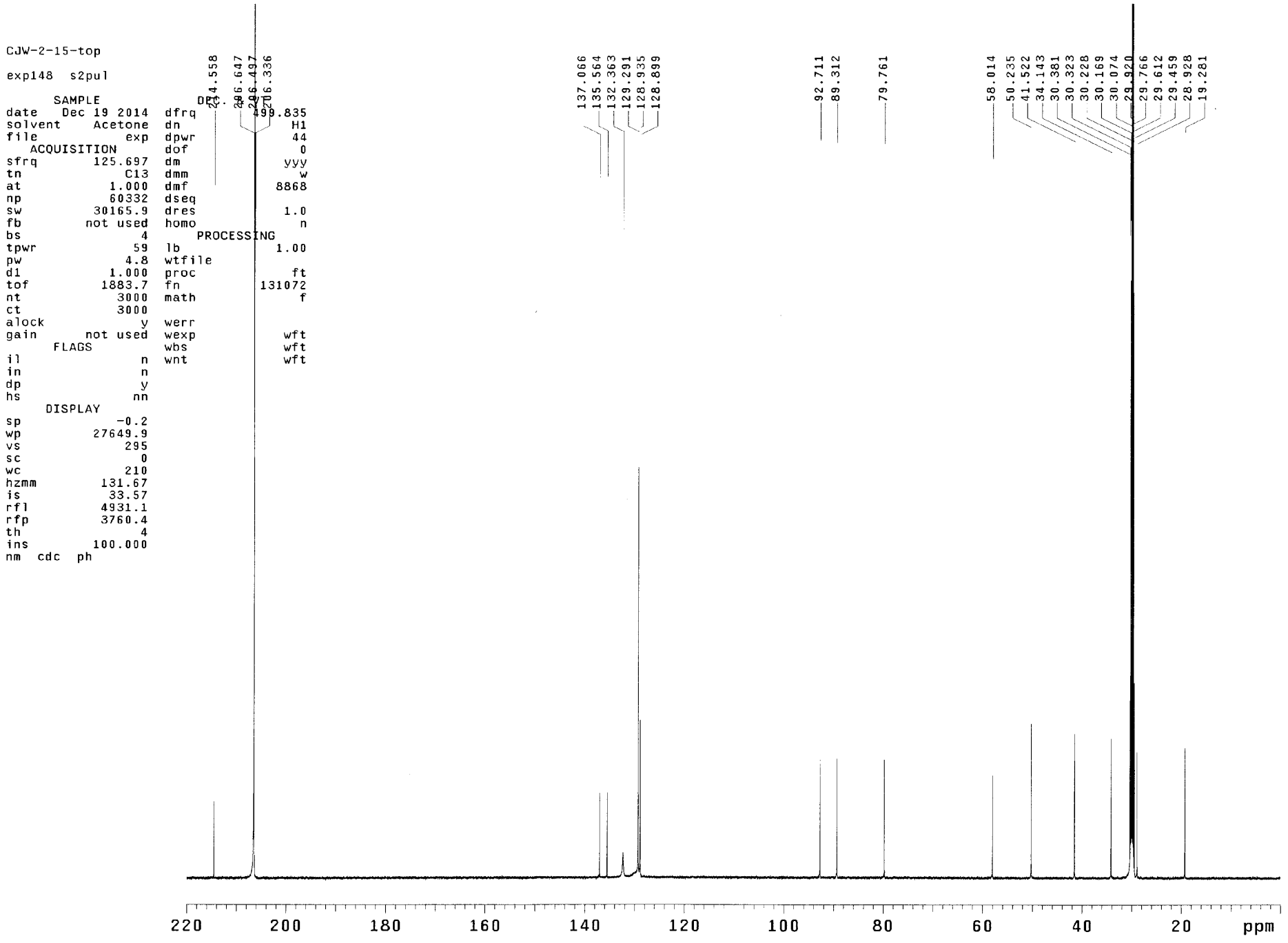


Fig S28. 13C NMR (acetone-d6, 125 MHz) of compound 3a.

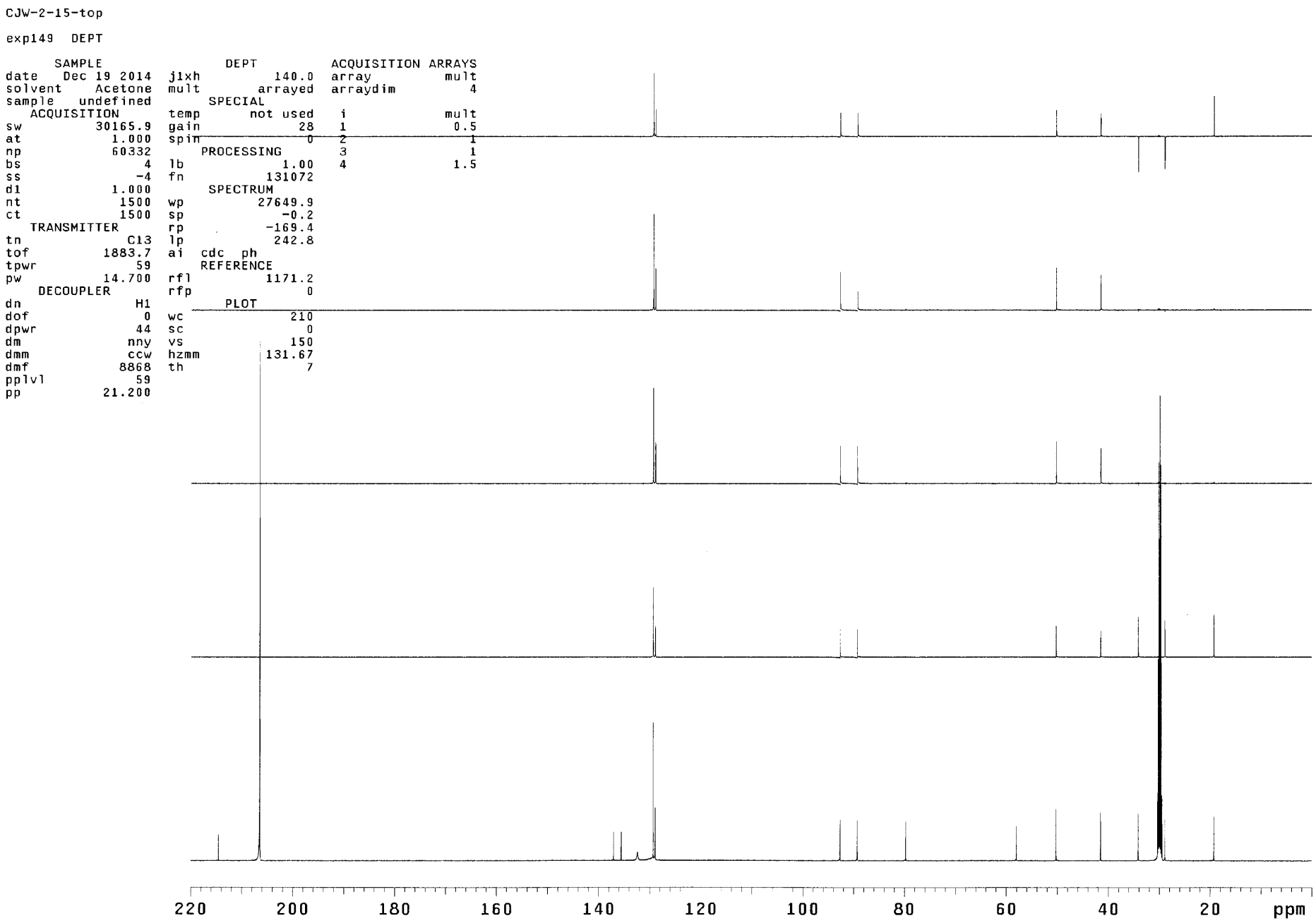


Fig S29. DEPT of compound 3a.

Fig S30. HSQC of compound 3a.

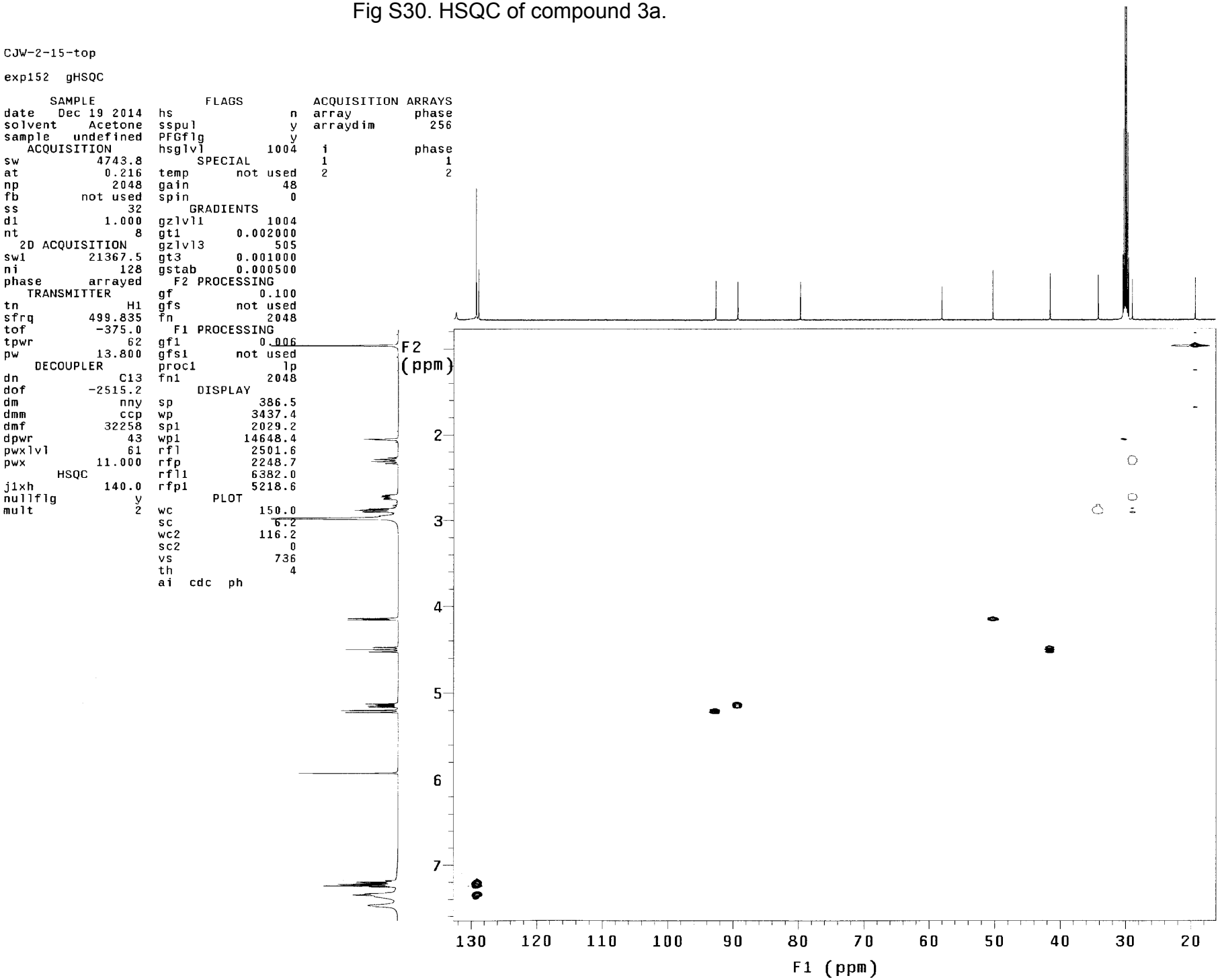


Fig S31. COSY of compound 3a.

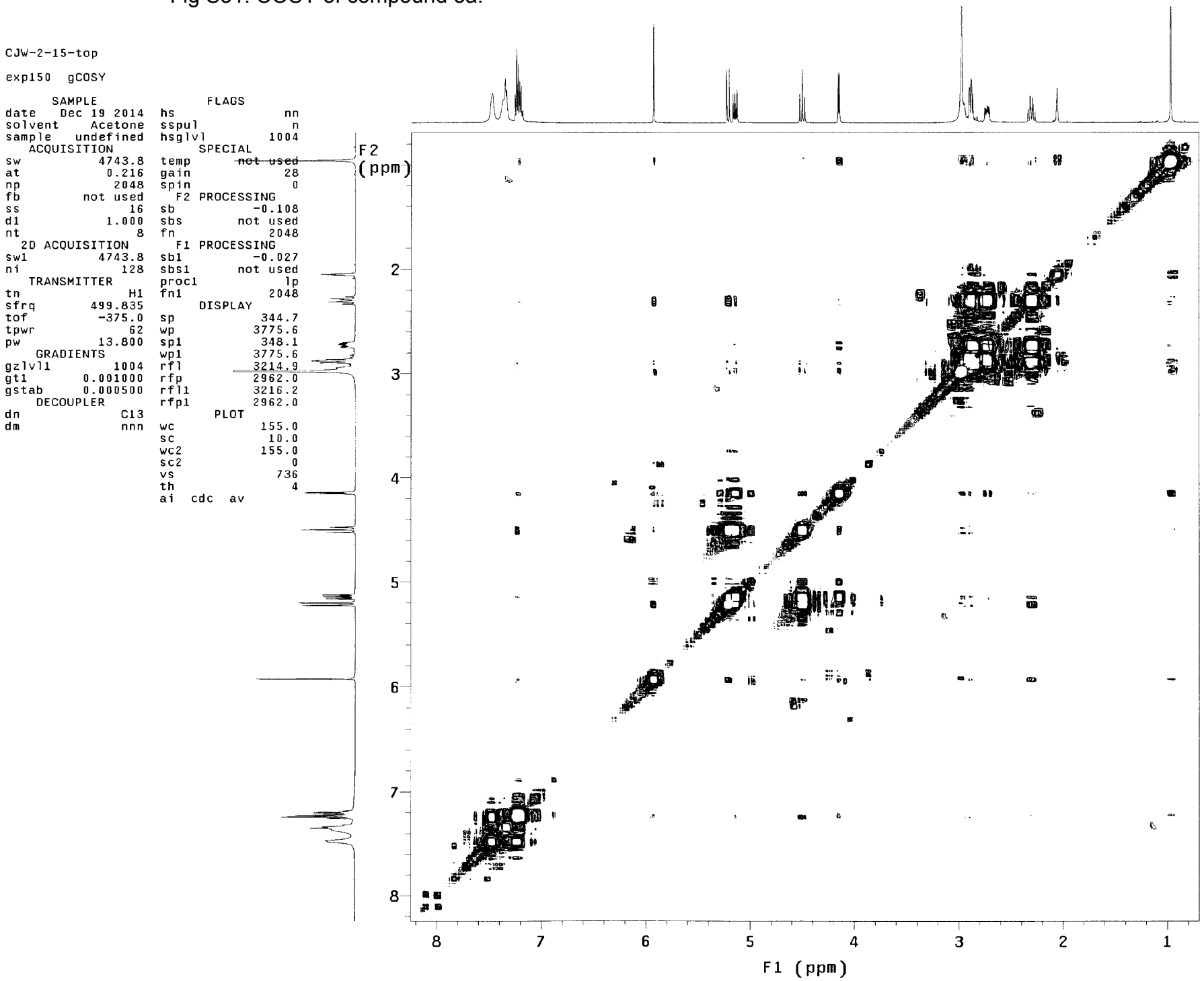


Fig S32. NOESY of compound 3a.

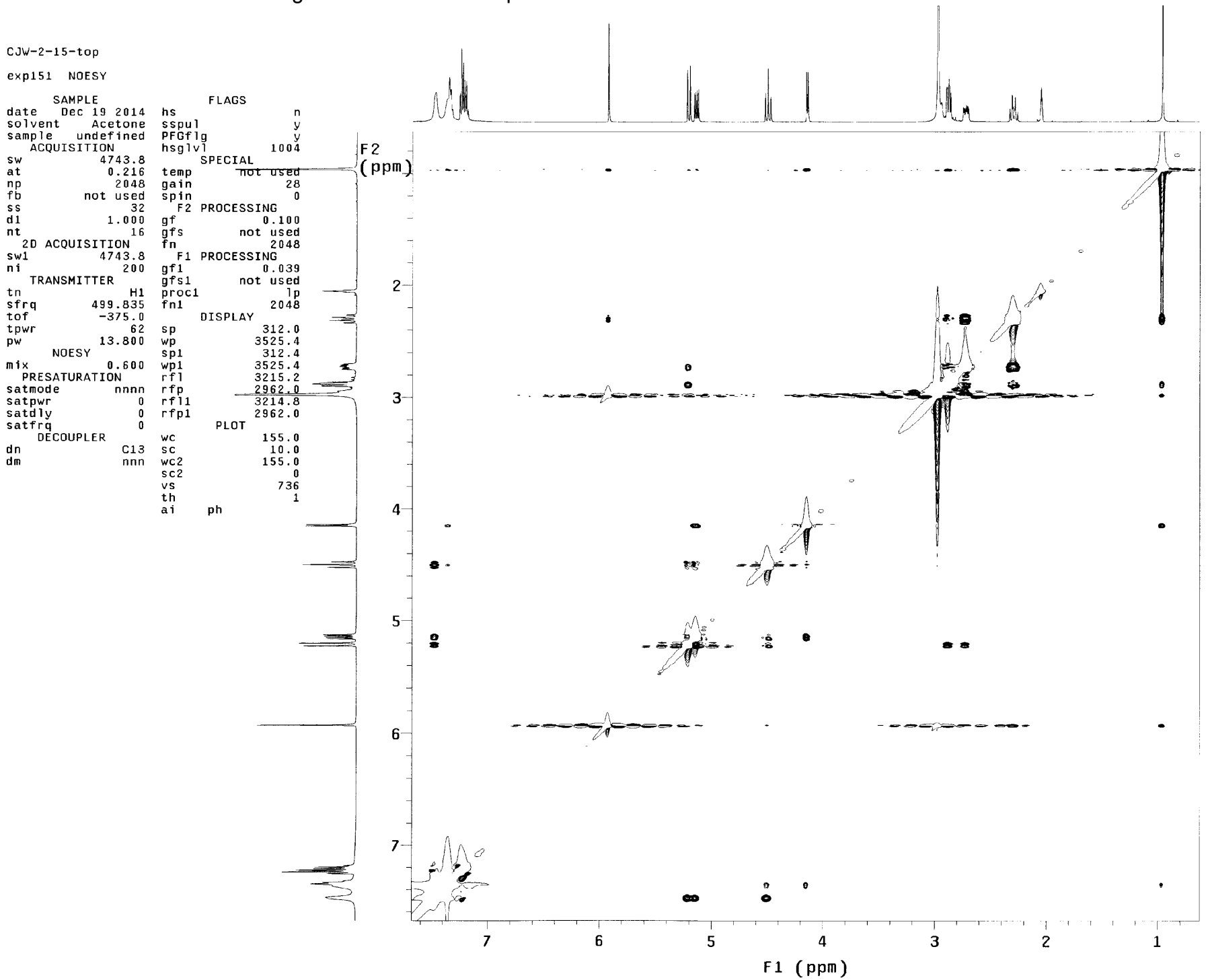


Fig S33. 1H NMR (acetone-d6, 500 MHz) of compound 5a.

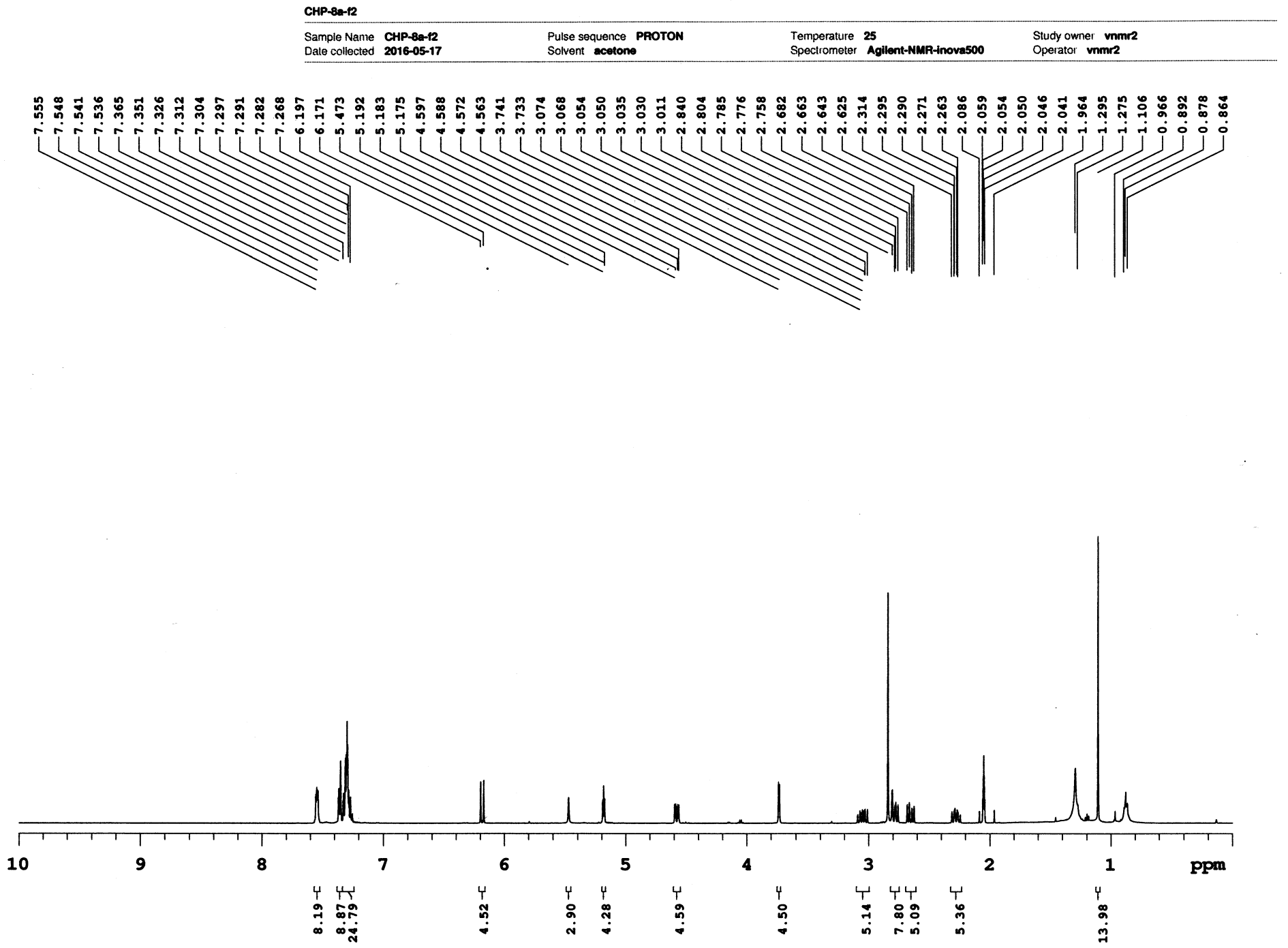
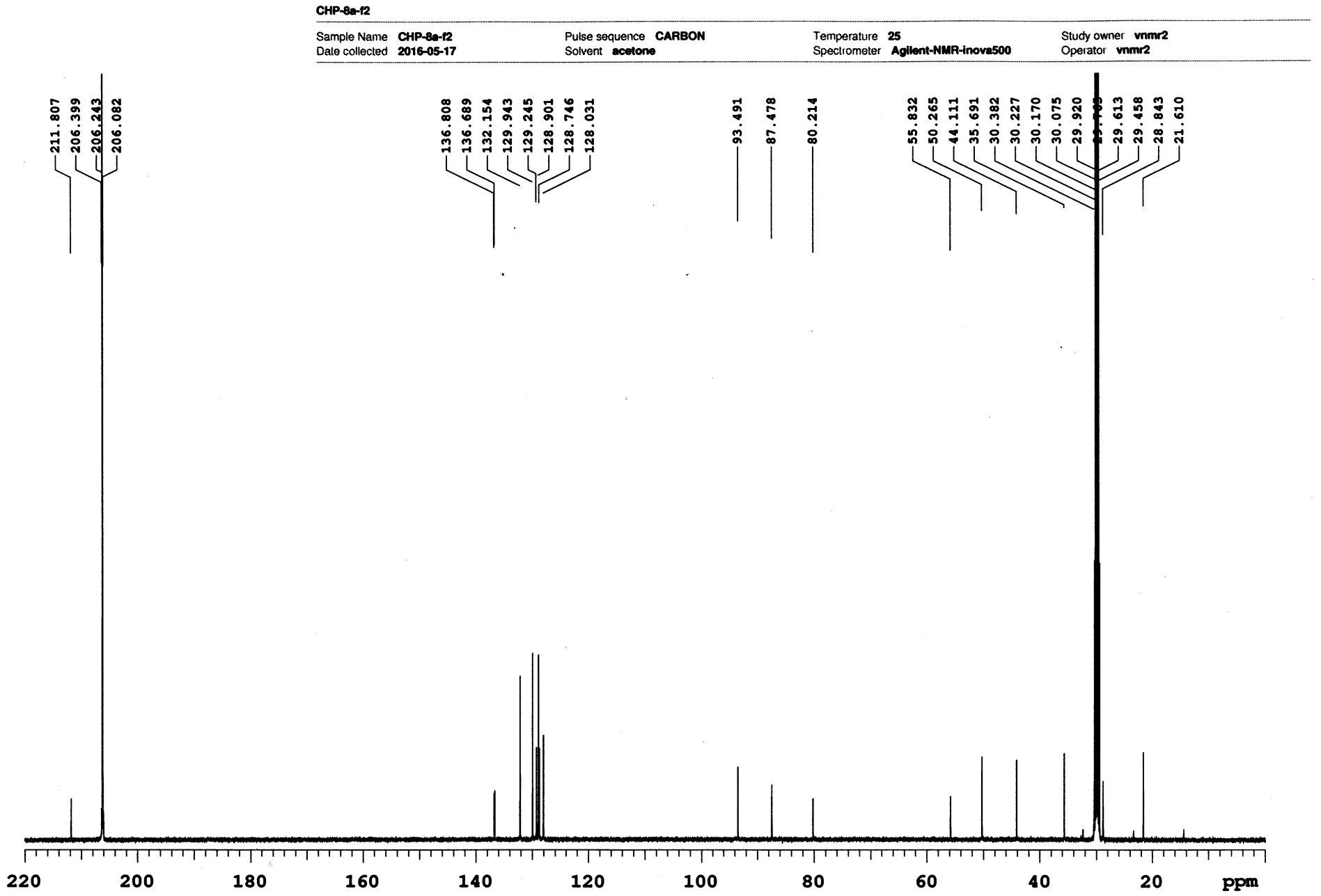


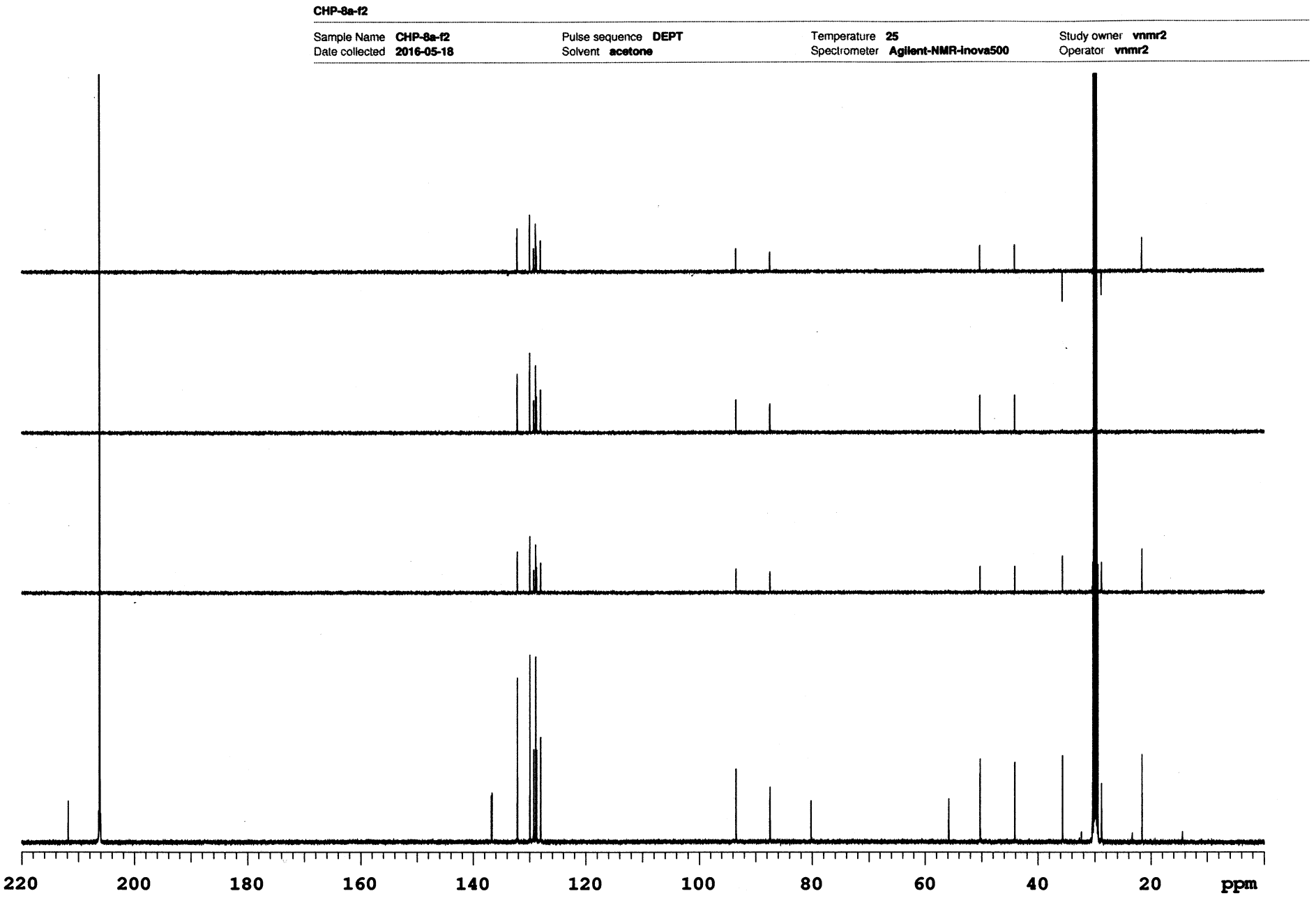
Fig S34. 13C NMR (acetone-d6, 125 MHz) of compound 5a.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8a-f2/CARBON_02

Plot date 2016-05-18

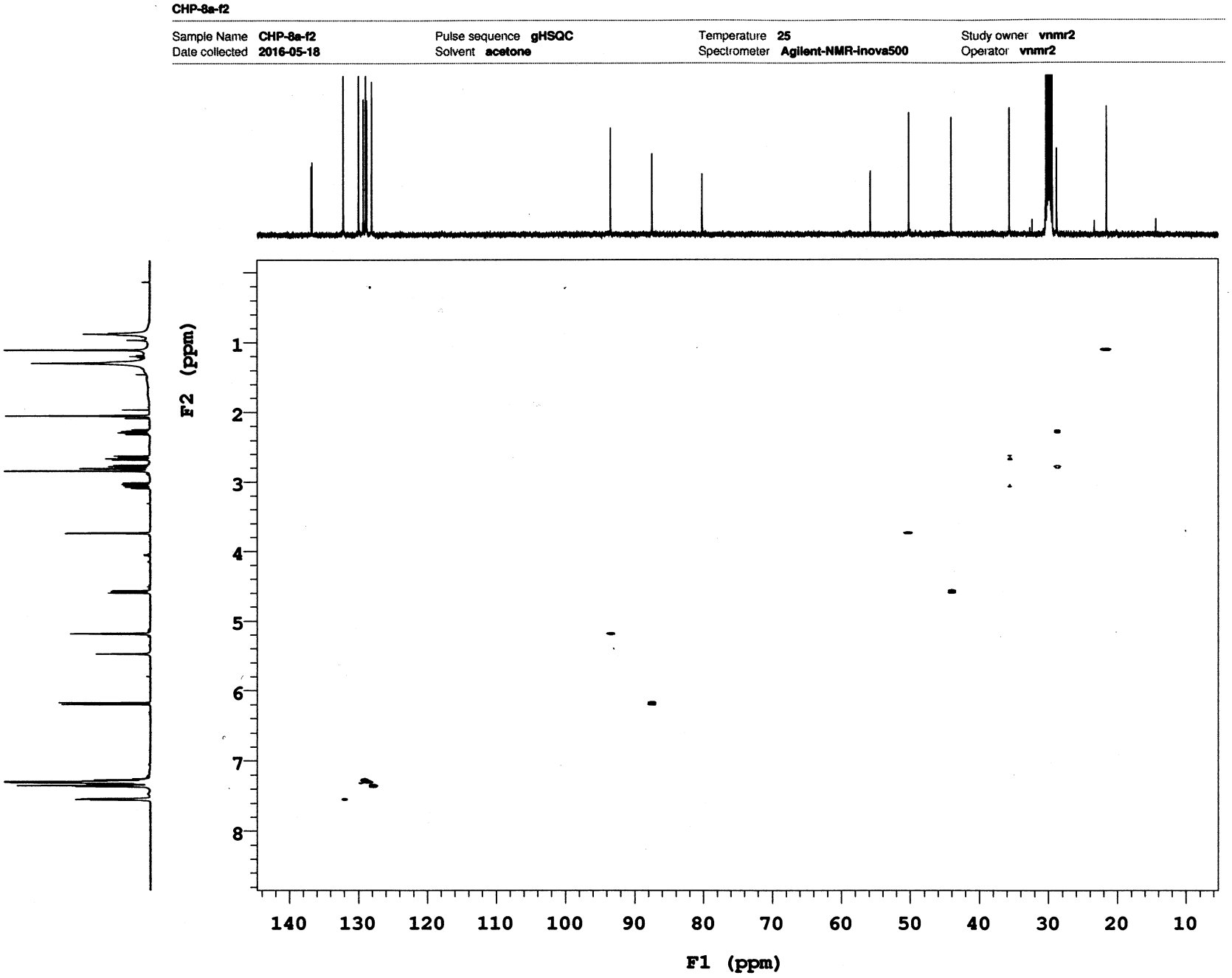
Fig S35. DEPT of compound 5a.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8a-f2/DEPT_01

Plot date 2016-05-18

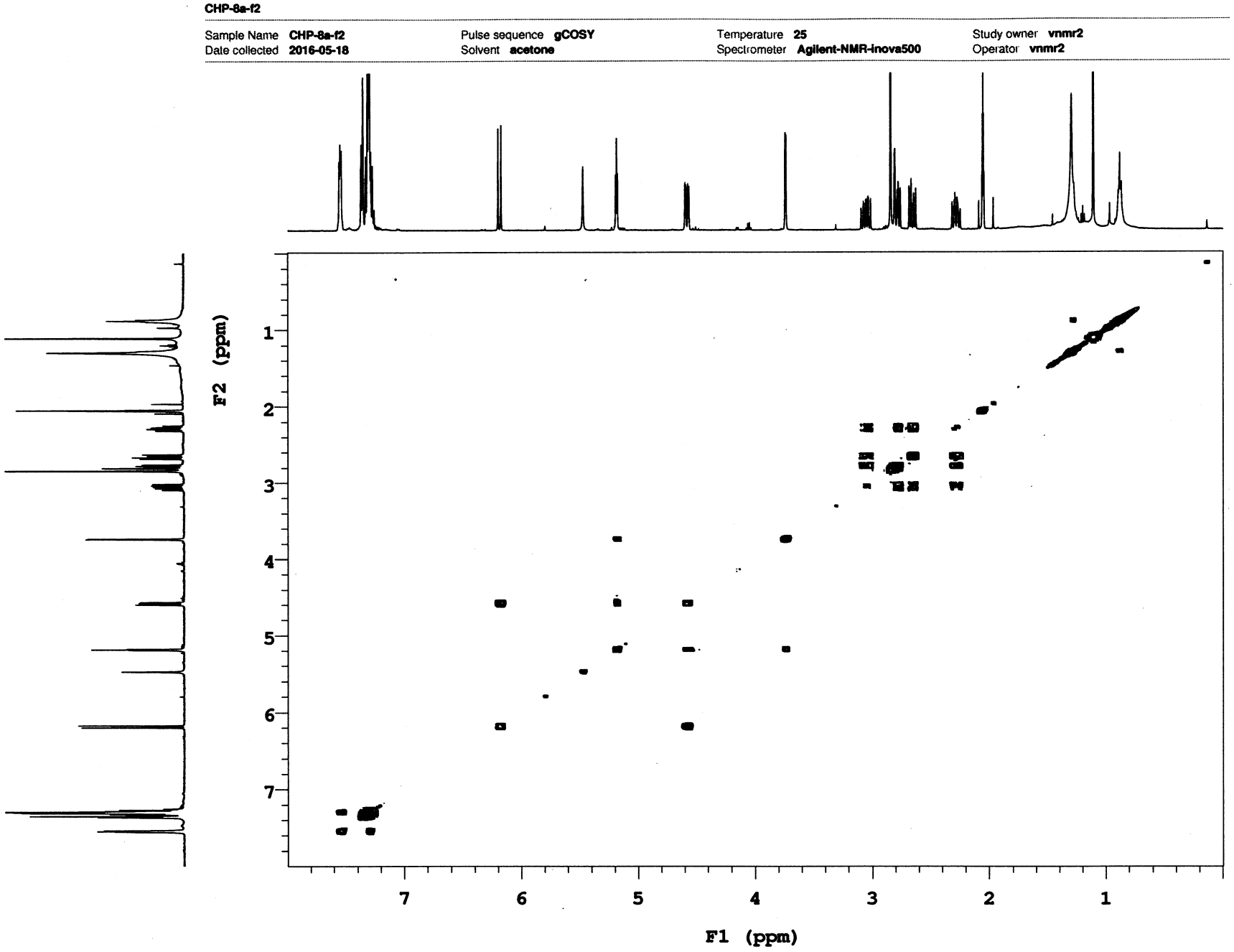
Fig S36. HSQC of compound 5a.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8a-f2/gHSQC_01

Plot date 2016-05-18

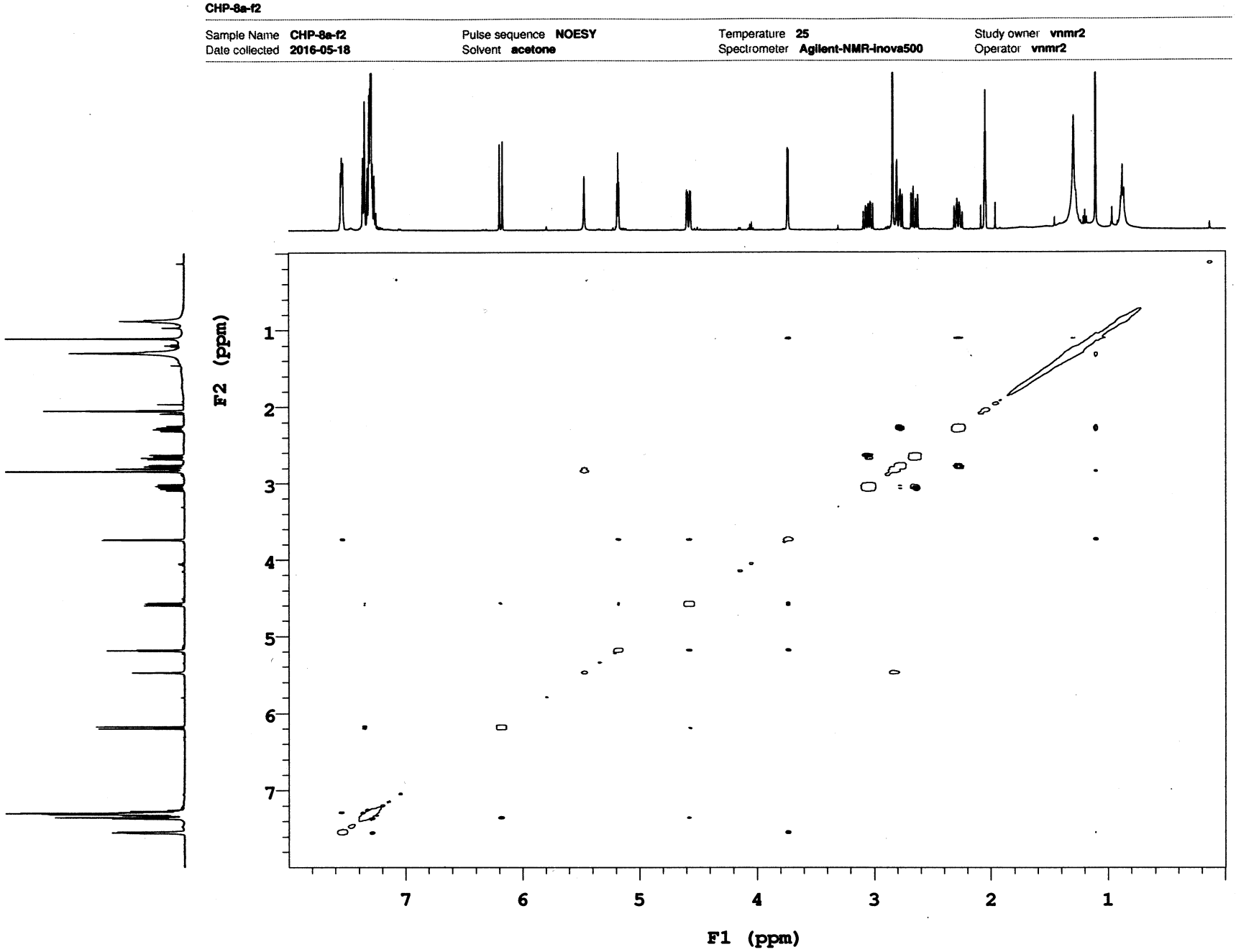
Fig S37. COSY of compound 5a.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8a-f2/gCOSY_01

Plot date 2016-05-18

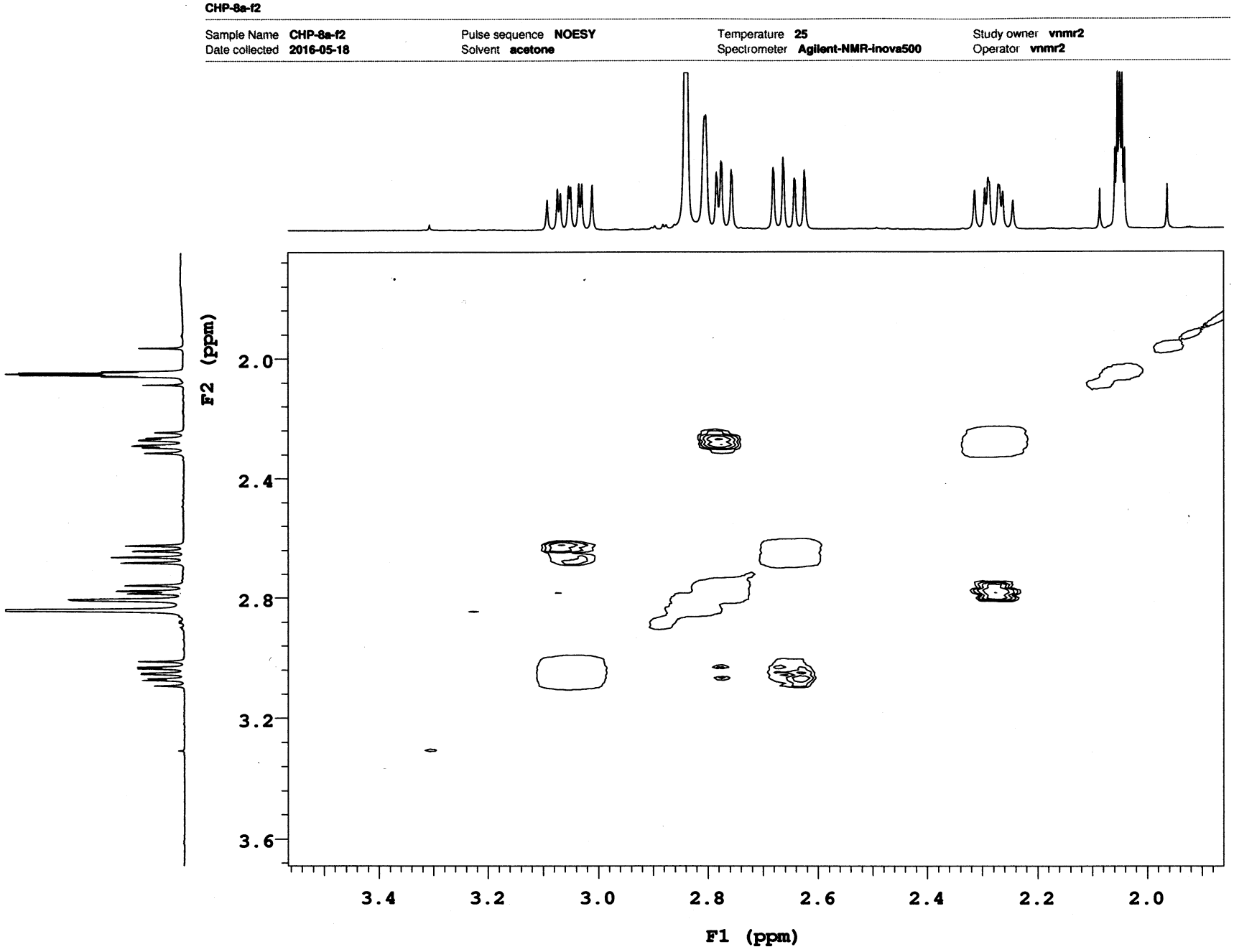
Fig S38. NOESY of compound 5a.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8a-f2/NOESY_01

Plot date 2016-05-18

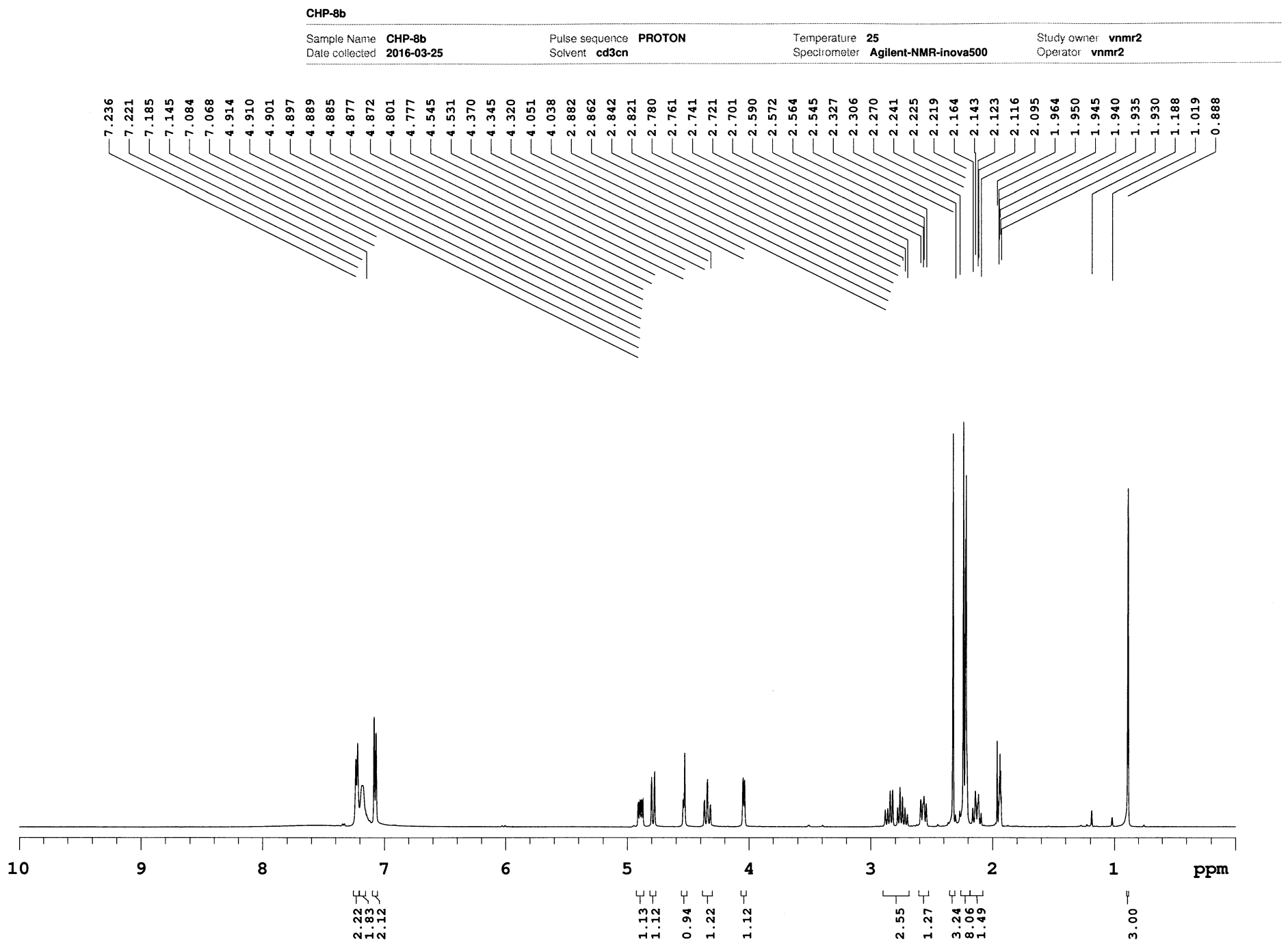
Fig S39. NOESY of compound 5a, expanded.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8a-f2/NOESY_01

Plot date 2016-05-18

Fig S40. 1H NMR (CD3CN, 500 MHz) of compound 3b.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b/PROTON_09

Plot date 2016-03-29

Fig S41. 13C NMR (CD3CN, 125 MHz) of compound 3b.

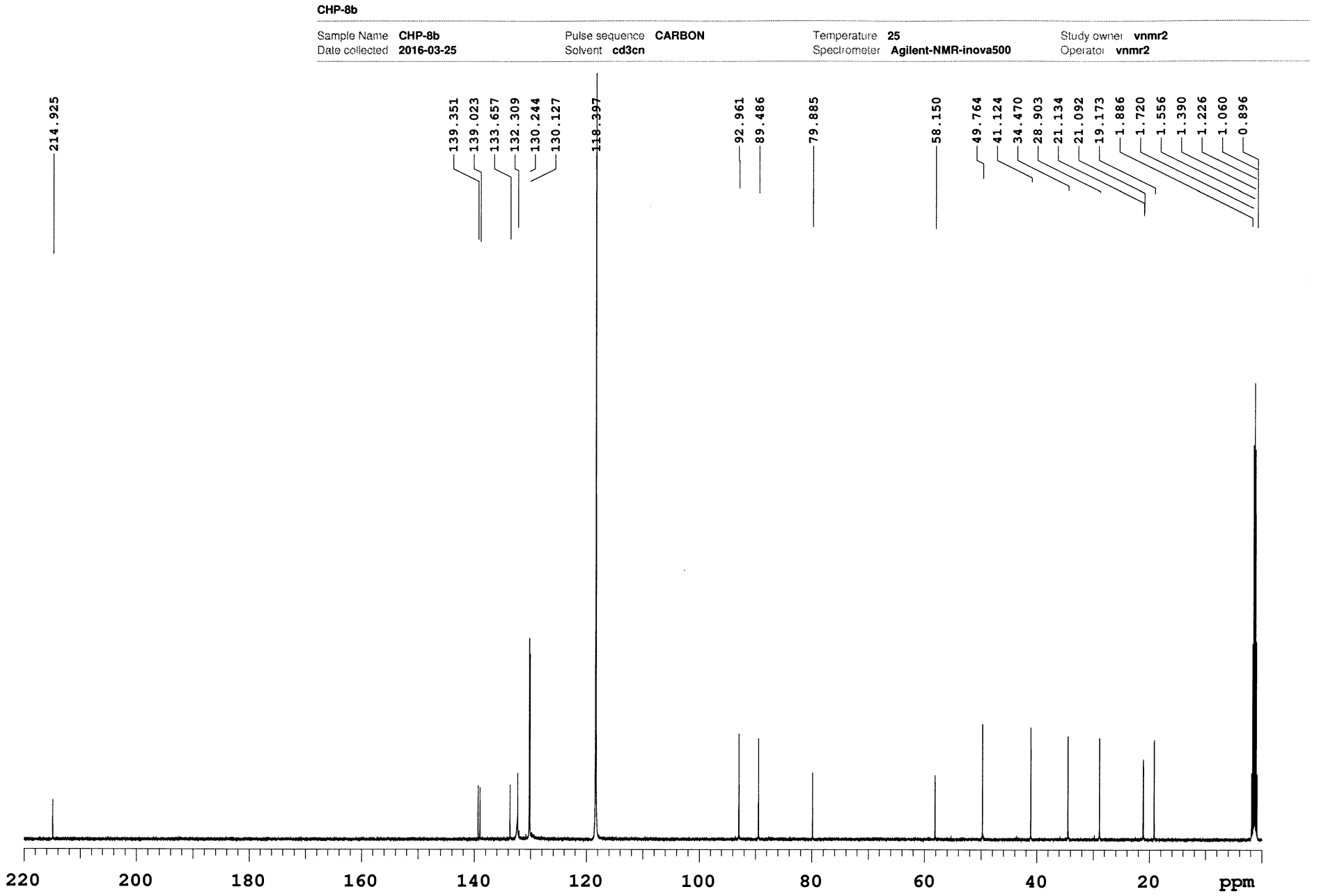


Fig S42. DEPT of compound 3b.

CHP-8b

Sample Name **CHP-8b**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2016-03-25**	Solvent **cd3cn**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**

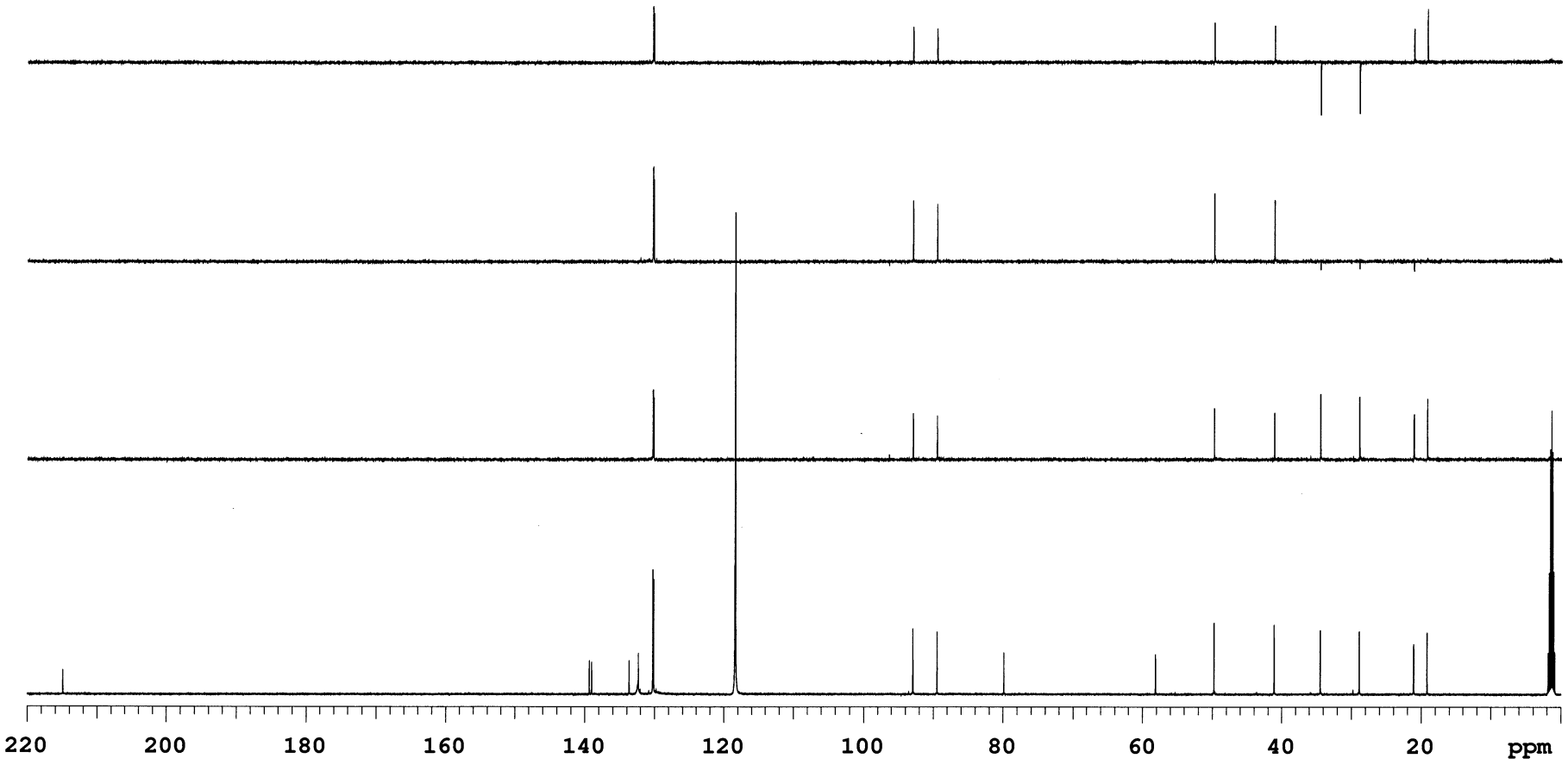
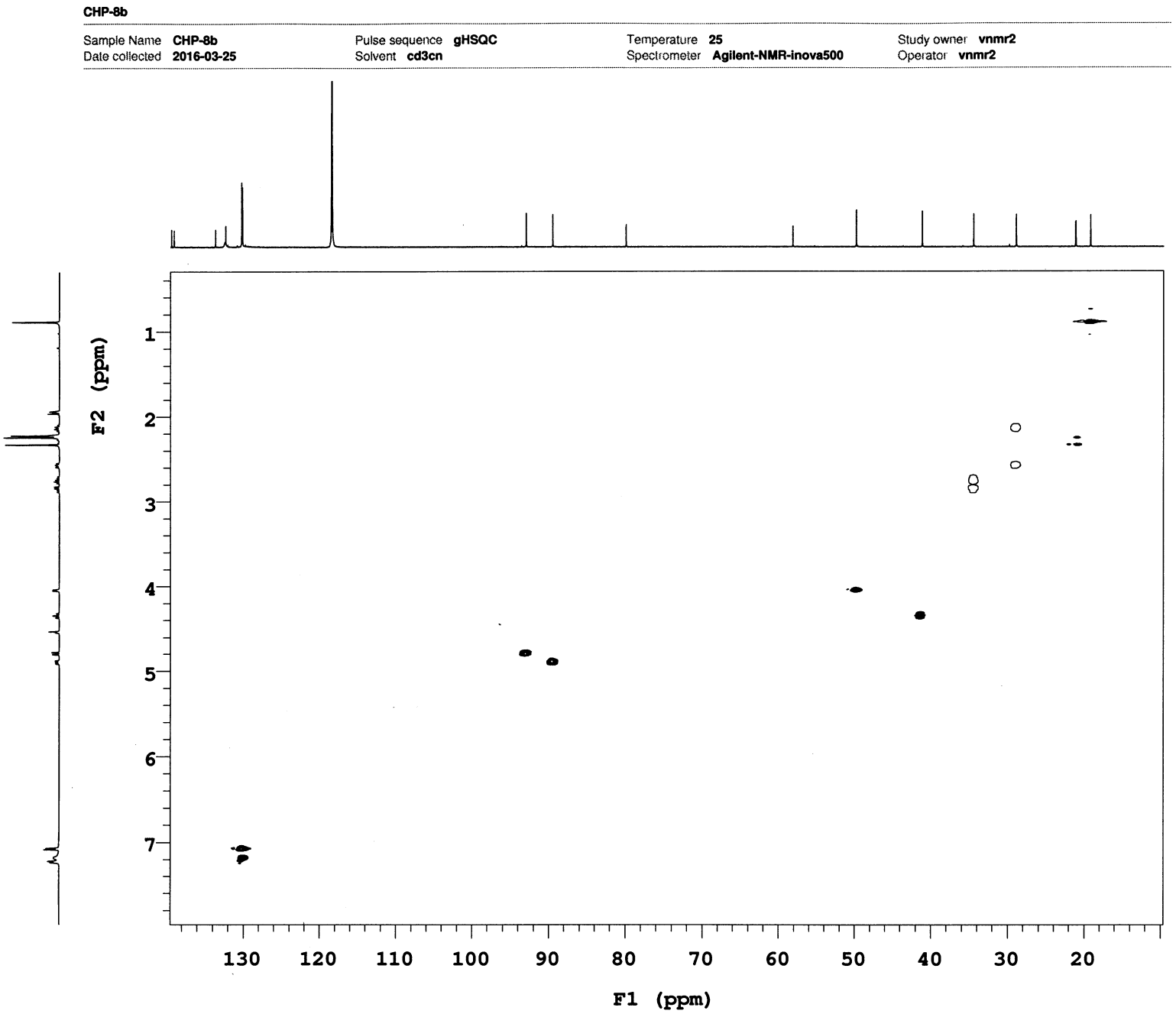


Fig S43. HSQC of compound 3b.



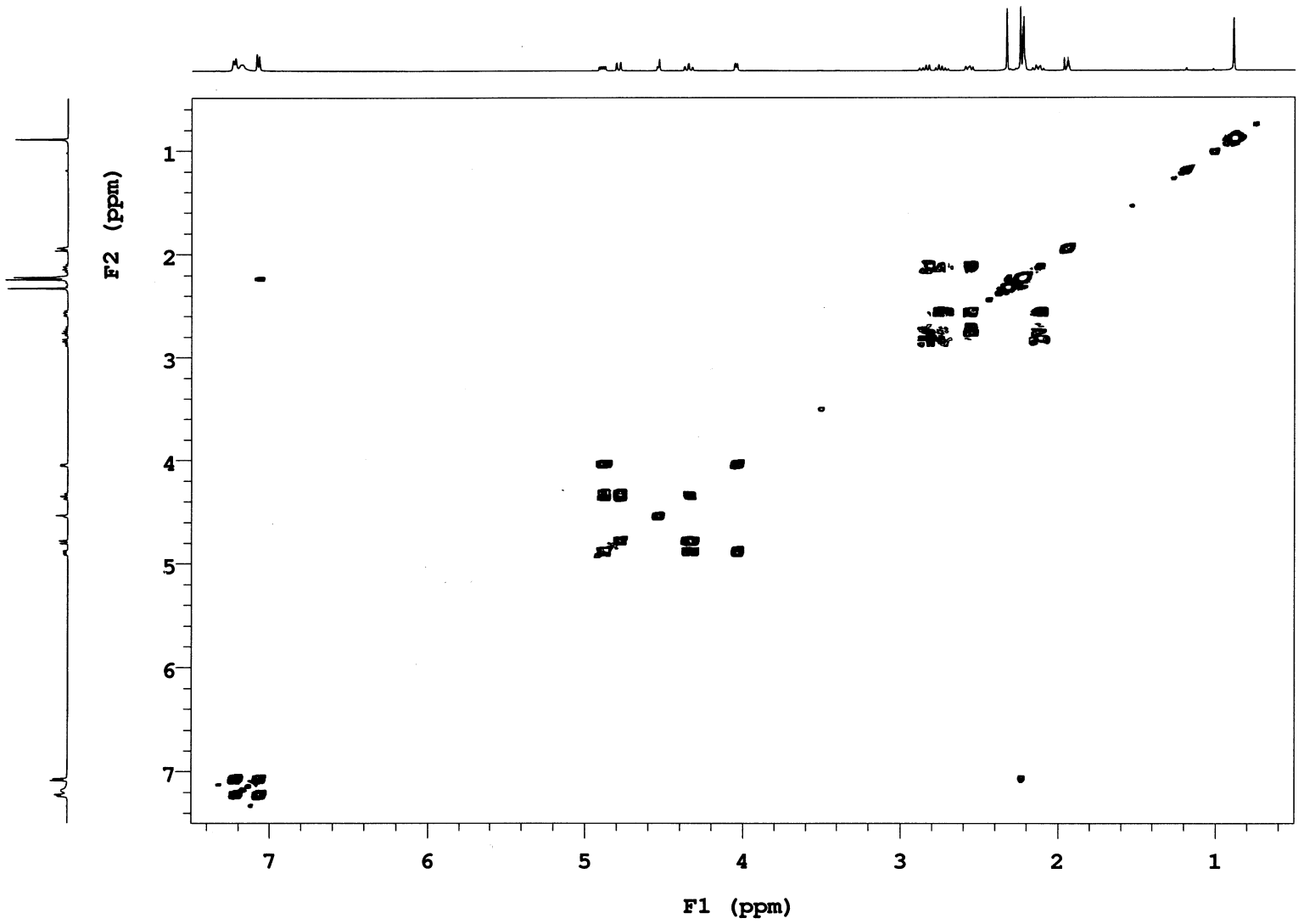
Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b/gHSQC_01

Plot date 2016-03-29

Fig S44. COSY of compound 3b.

CHP-8b

Sample Name	**CHP-8b**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-03-25**	Solvent	**cd3cn**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b/gCOSY_01

Plot date 2016-03-29

Fig S45. NOESY of compound 3b.

CHP-8b

Sample Name	**CHP-8b**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-03-25**	Solvent	**cd3cn**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**

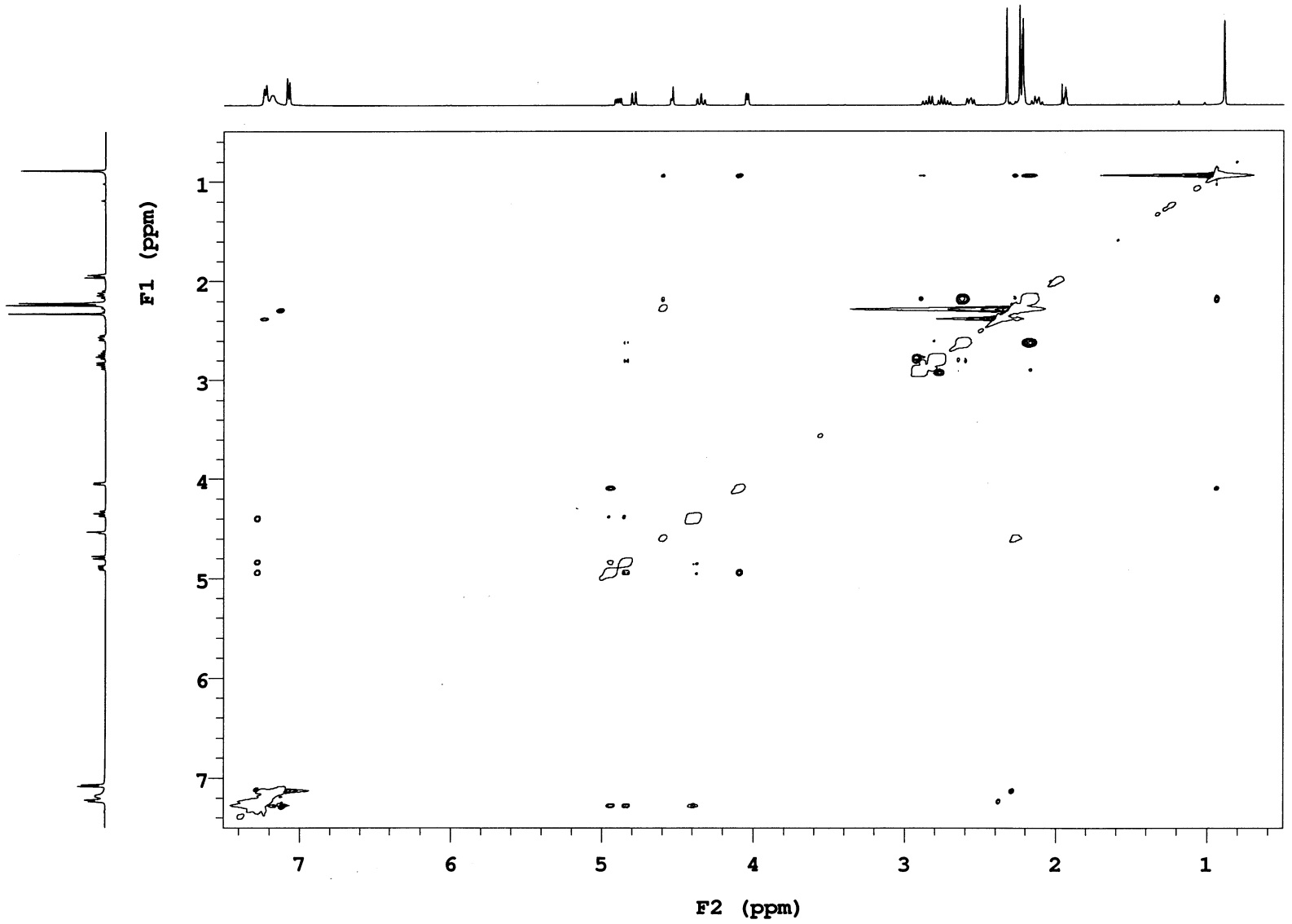
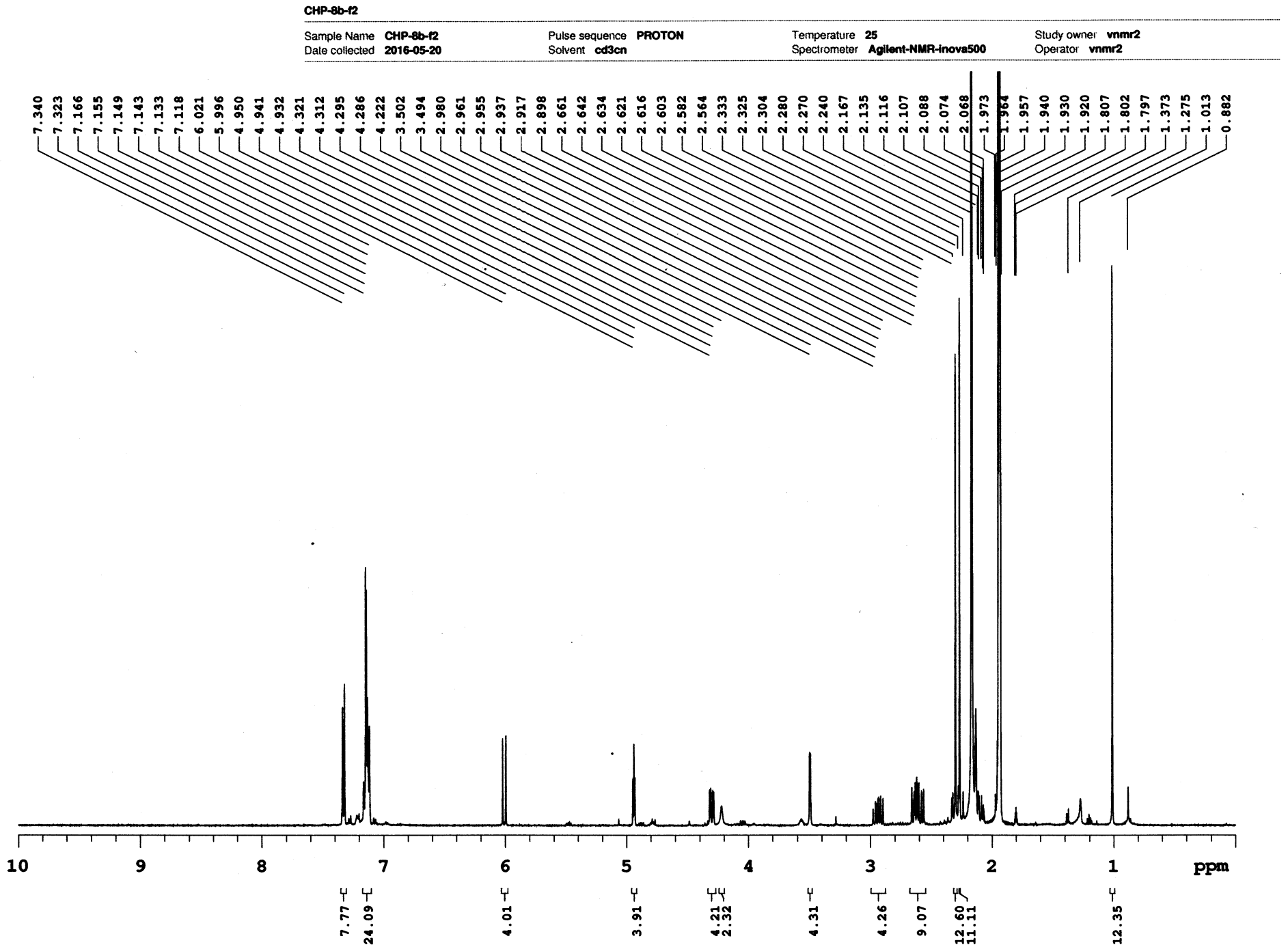


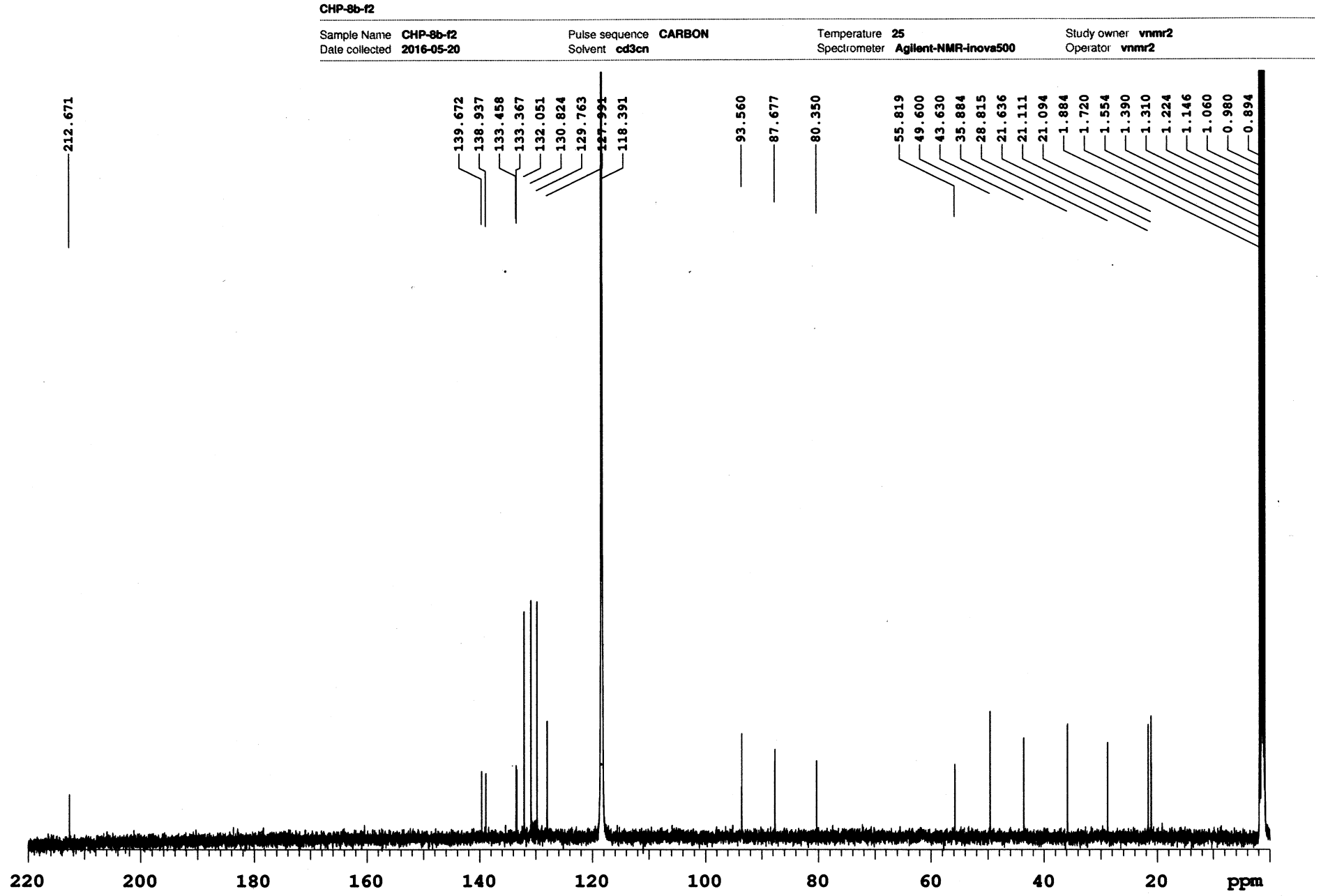
Fig S46. 1H NMR (CD3CN, 500 MHz) of compound 5b.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b-f2/PROTON_06

Plot date 2016-05-20

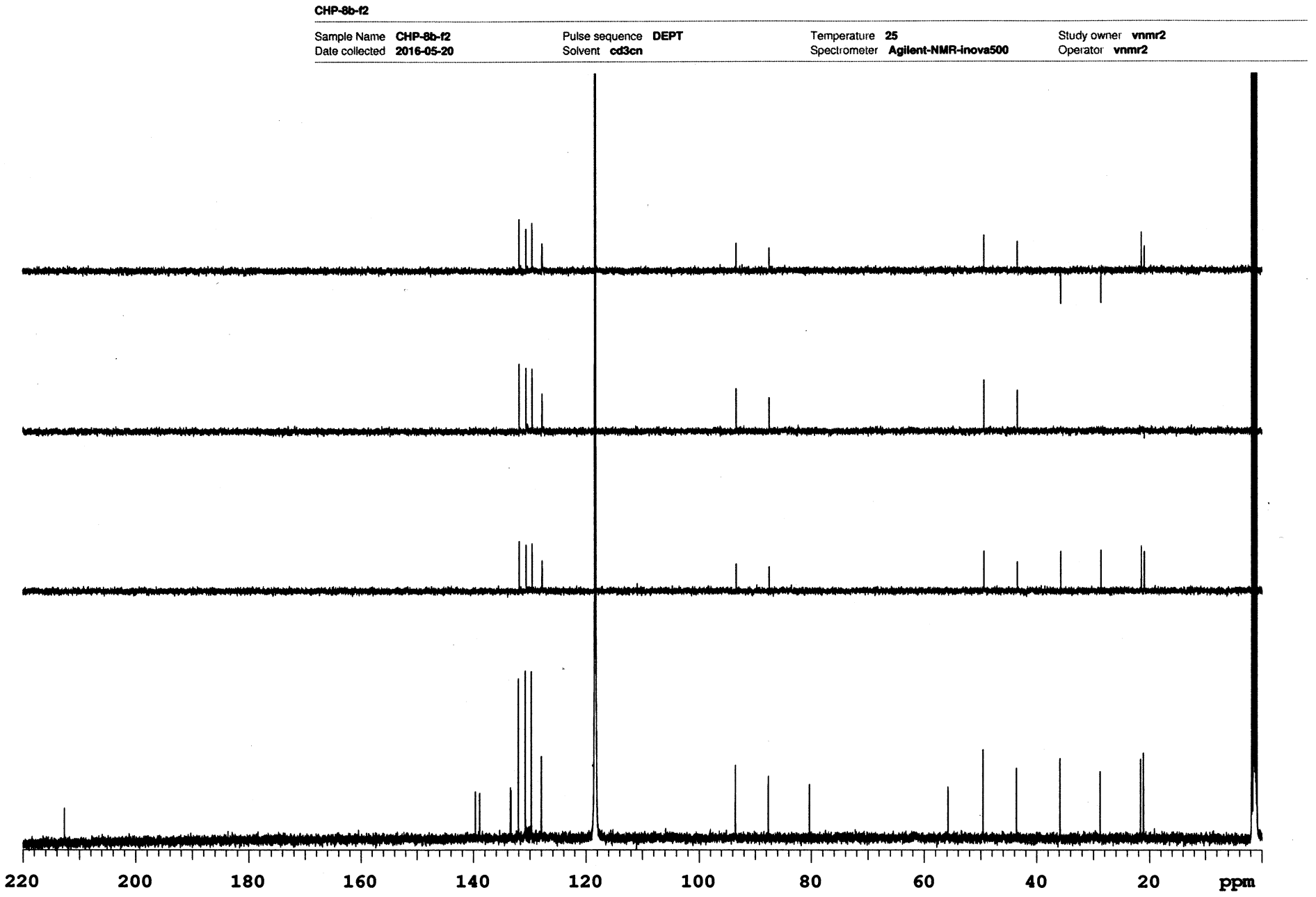
Fig S47. 13C NMR (CD3CN, 125 MHz) of compound 5b.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b-f2/CARBON_02

Plot date 2016-05-20

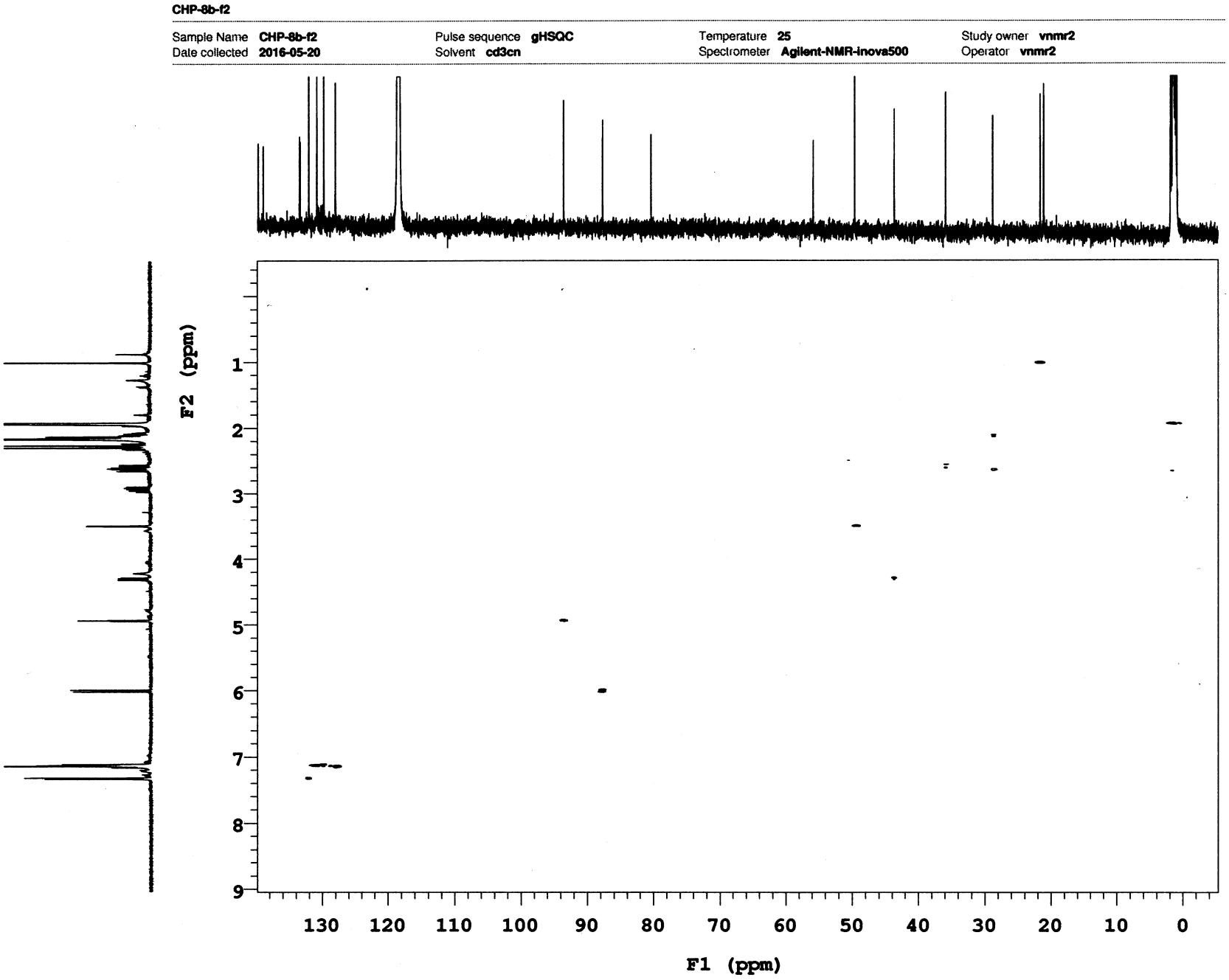
Fig S48. DEPT of compound 5b.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b-f2/DEPT_01

Plot date 2016-05-20

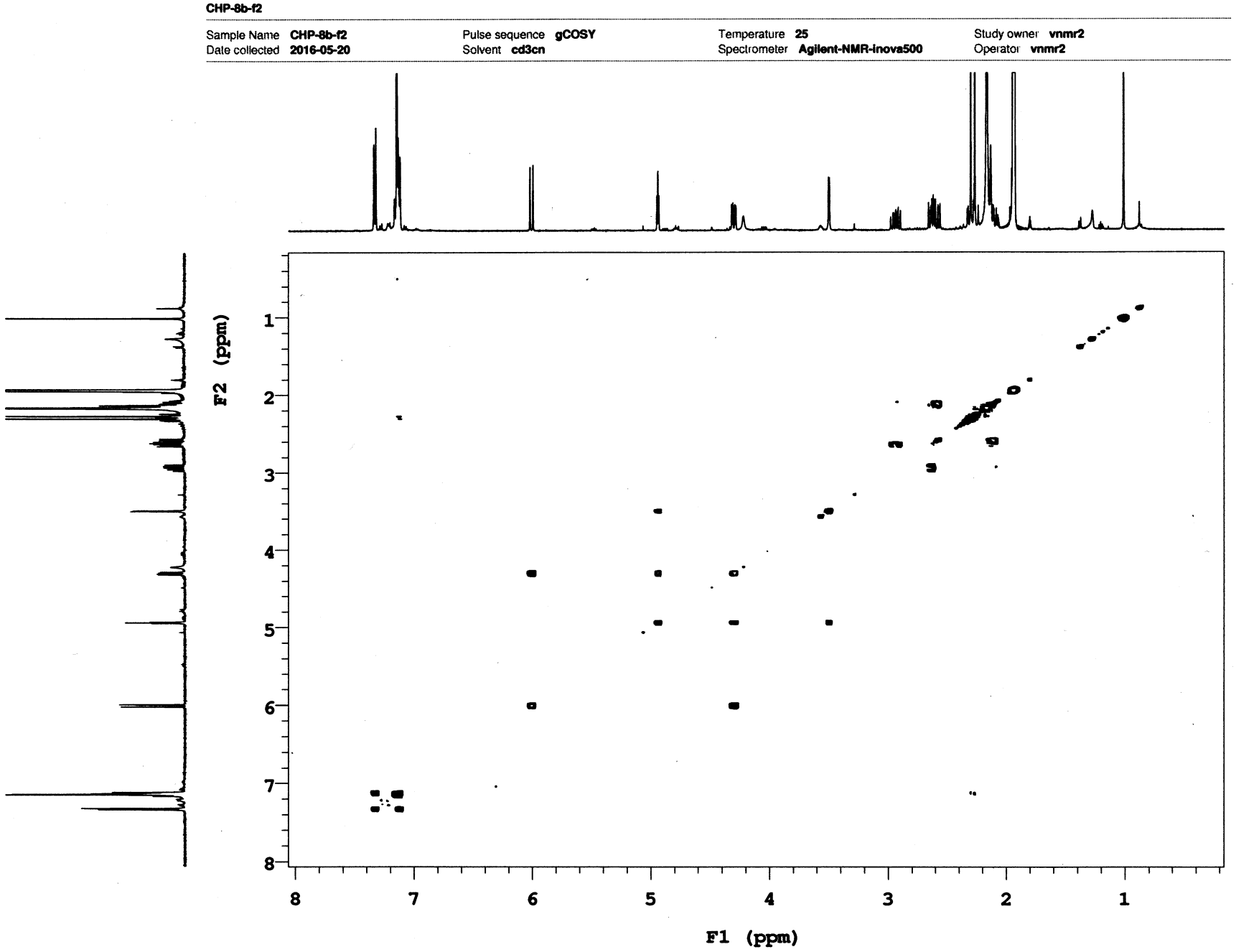
Fig S49. HSQC of compound 5b.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b-f2/gHSQC_01

Plot date 2016-05-20

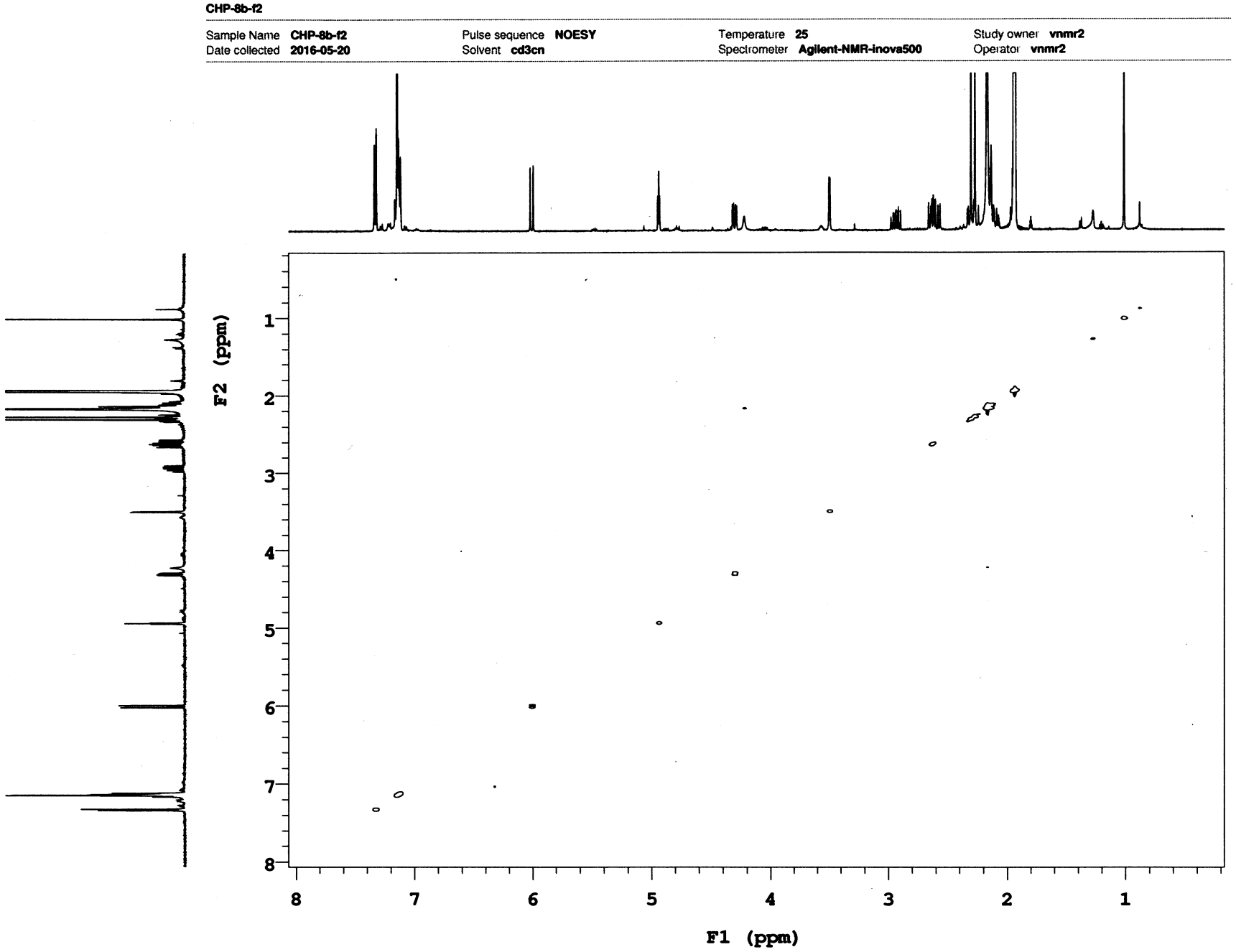
Fig S50. COSY of compound 5b.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b-f2/gCOSY_01

Plot date 2016-05-20

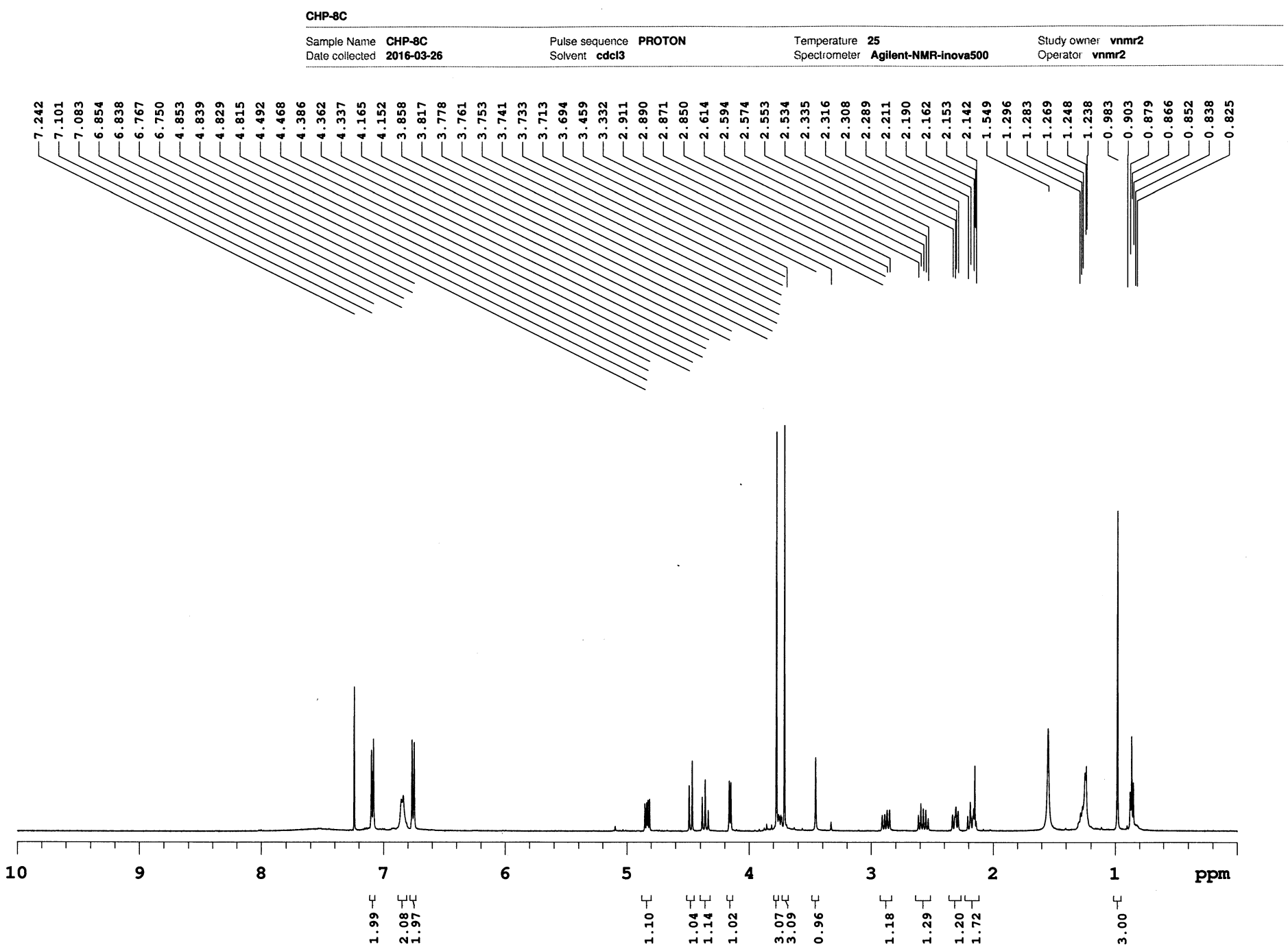
Fig S51. NOESY of compound 5b.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8b-f2/NOESY_01

Plot date 2016-05-20

Fig S52. 1H NMR (CDCl3, 500 MHz) of compound 3c.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8C/PROTON_04

Plot date 2016-03-29

Fig S53. 13C NMR (CDCl3, 125 MHz) of compound 3c.

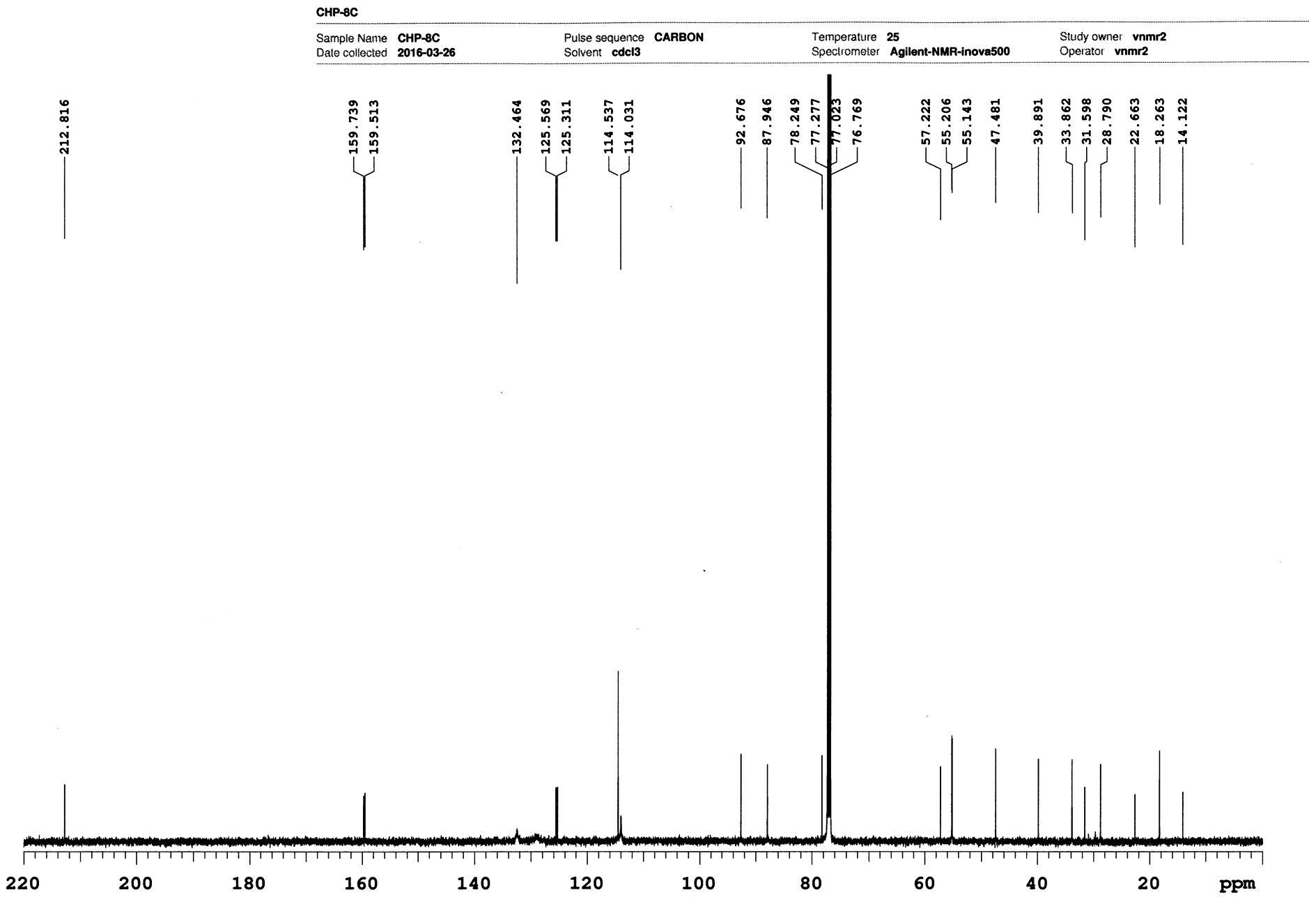
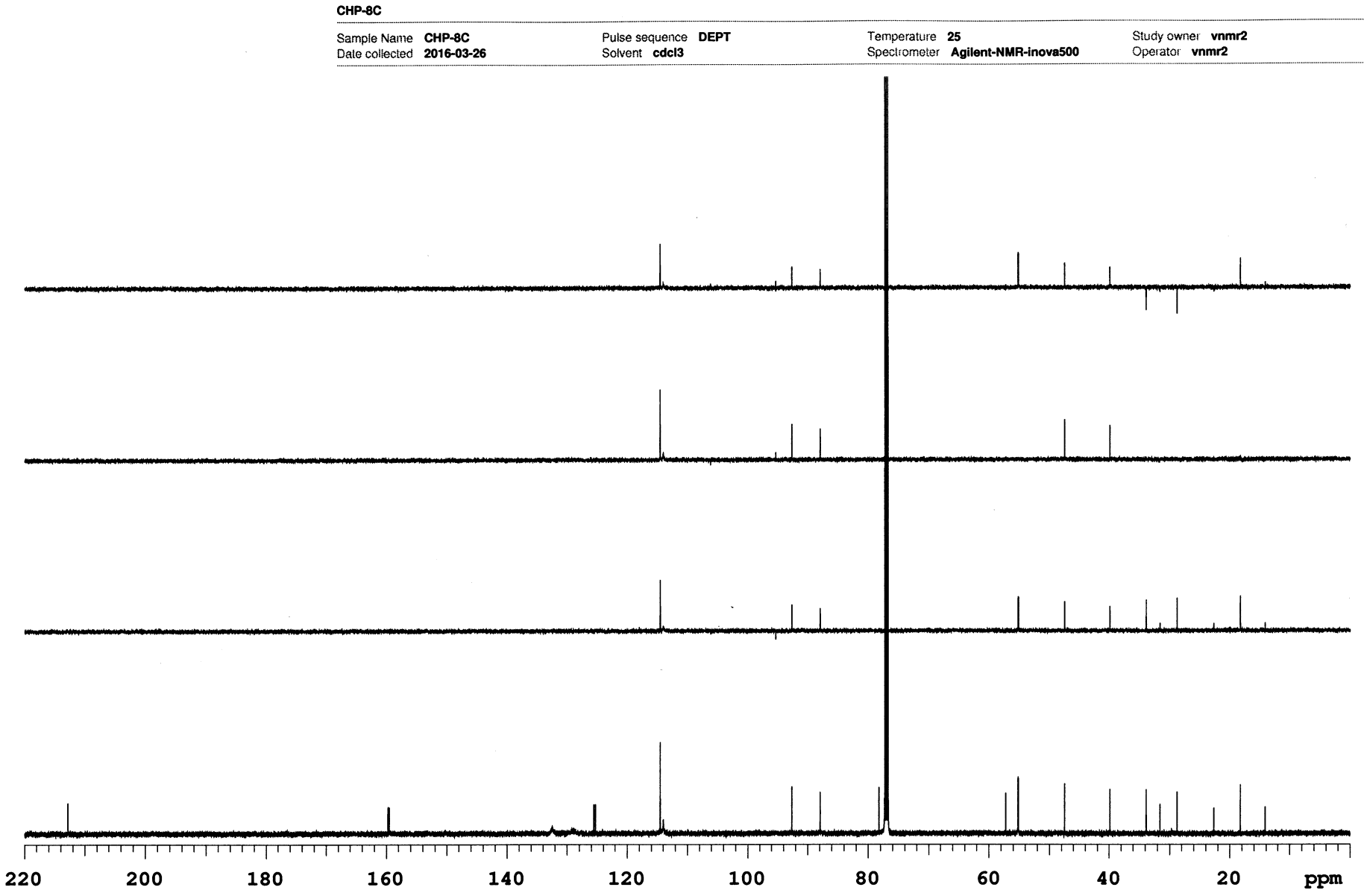


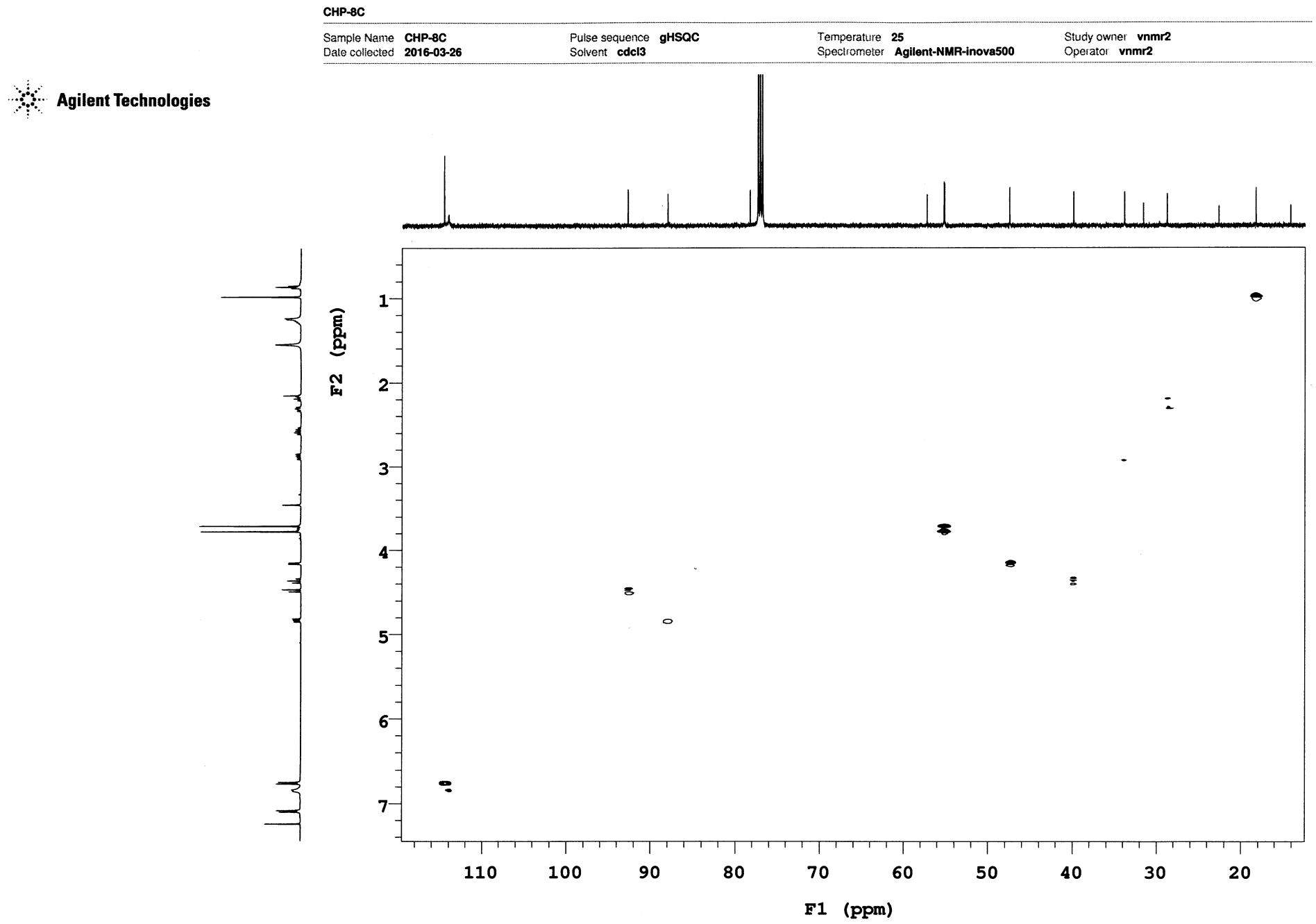
Fig S54. DEPT of compound 3c.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8C/DEPT_01

Plot date 2016-03-29

Fig S55. HSQC of compound 3c.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8C/gHSQC_01

Plot date 2016-03-29

Fig S56. COSY of compound 3c.

CHP-8C

Sample Name	**CHP-8C**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-03-26**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**

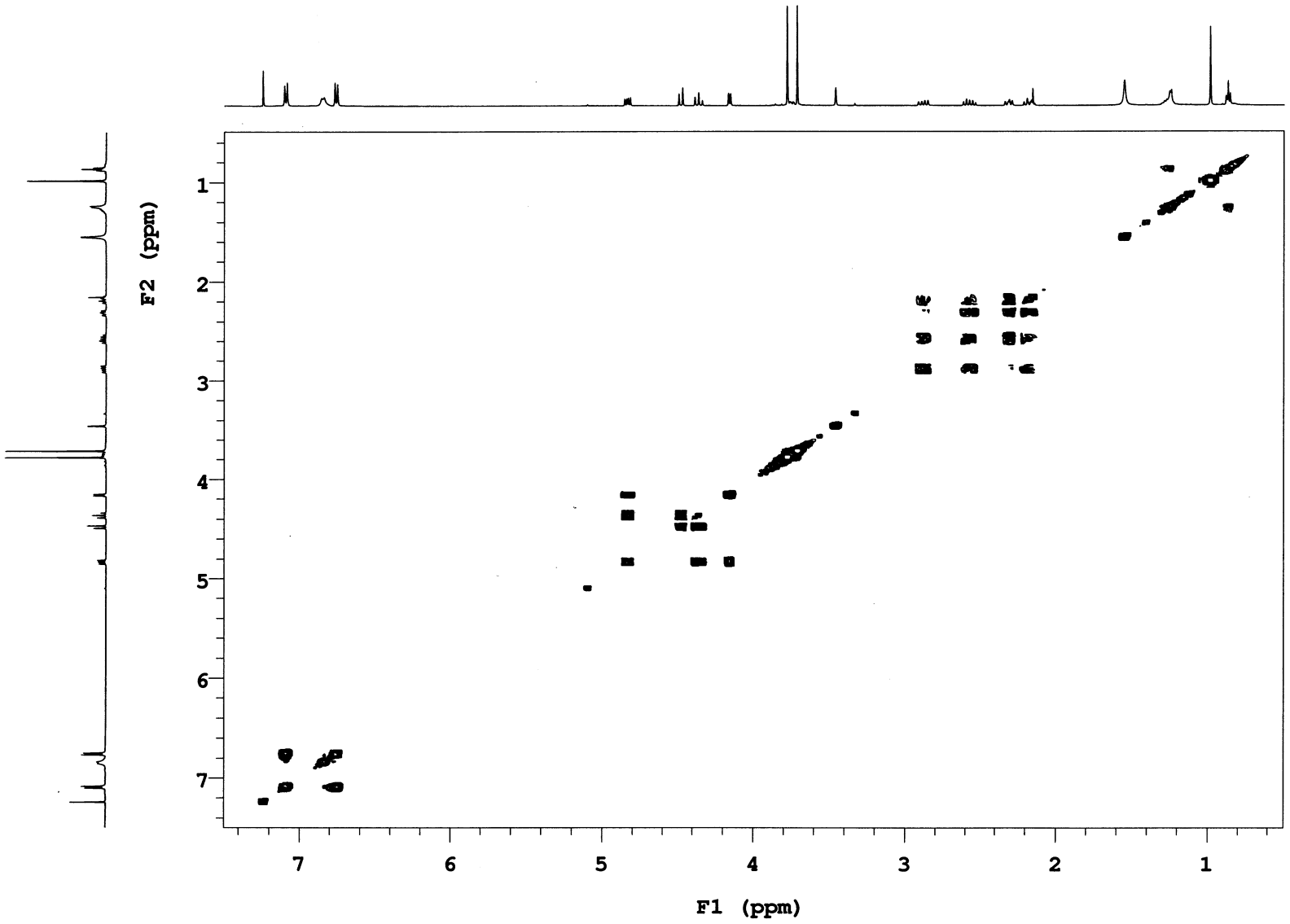


Fig S57. NOESY of compound 3c.

CHP-8C

Sample Name	**CHP-8C**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-03-26**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**

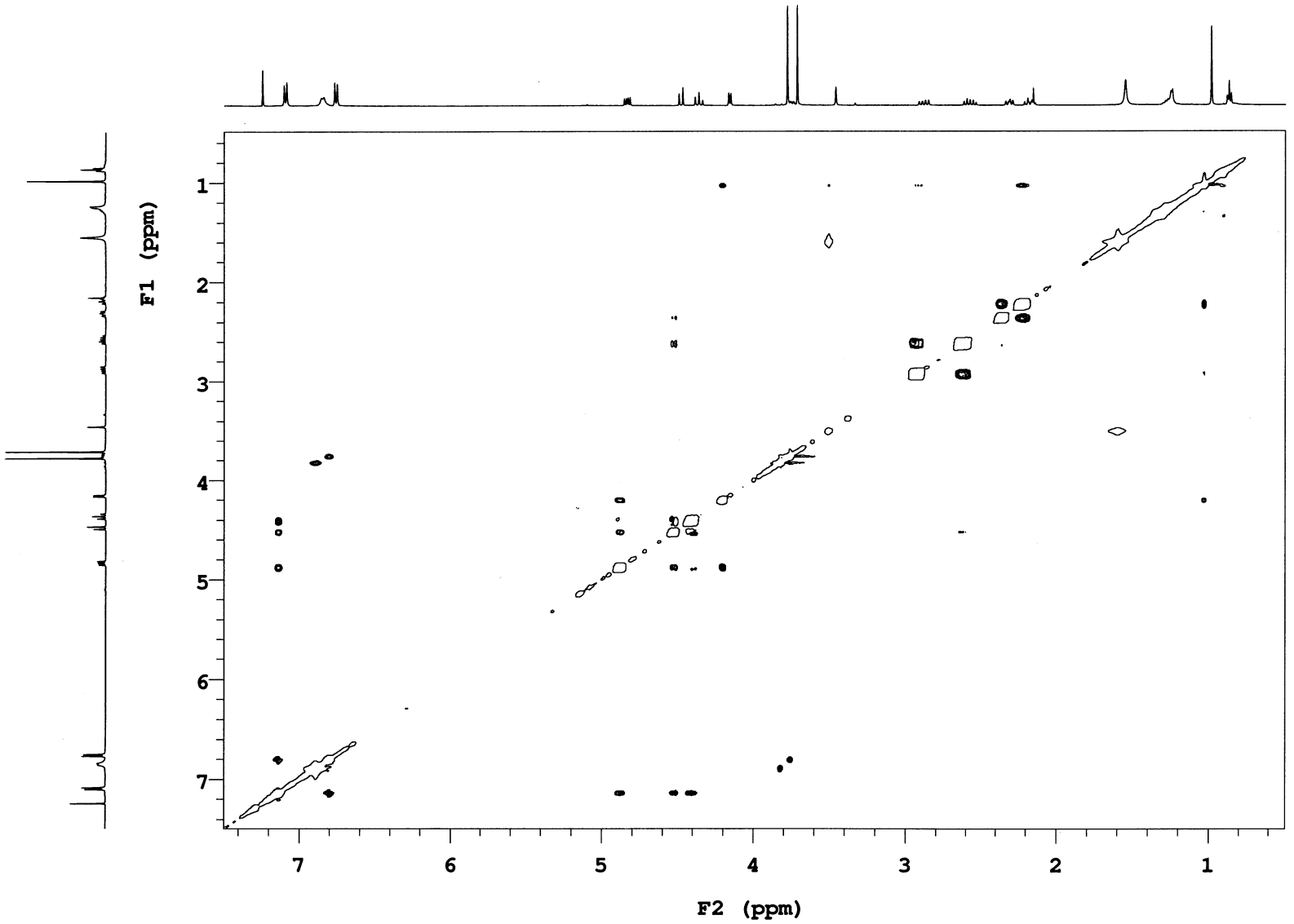
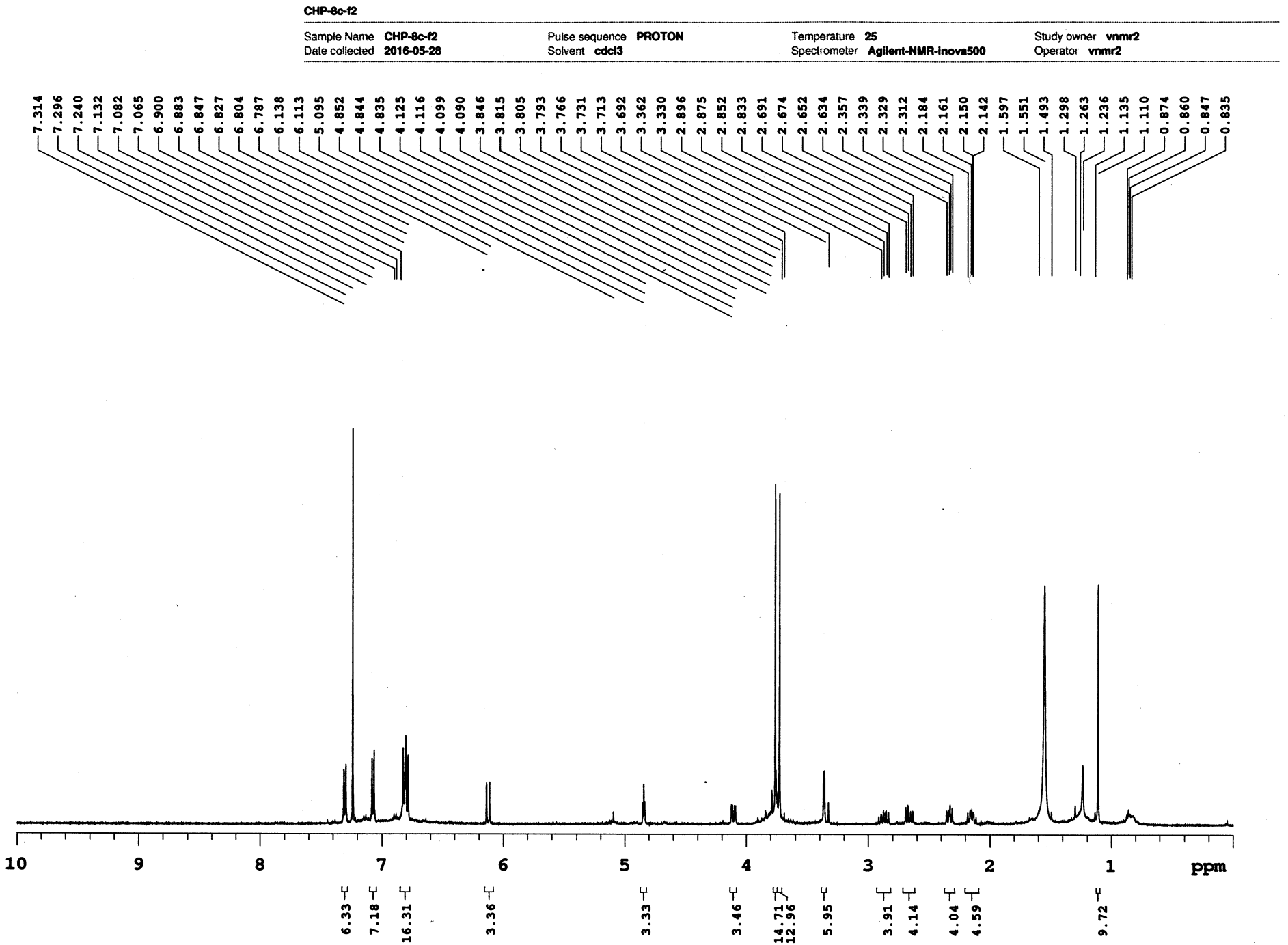


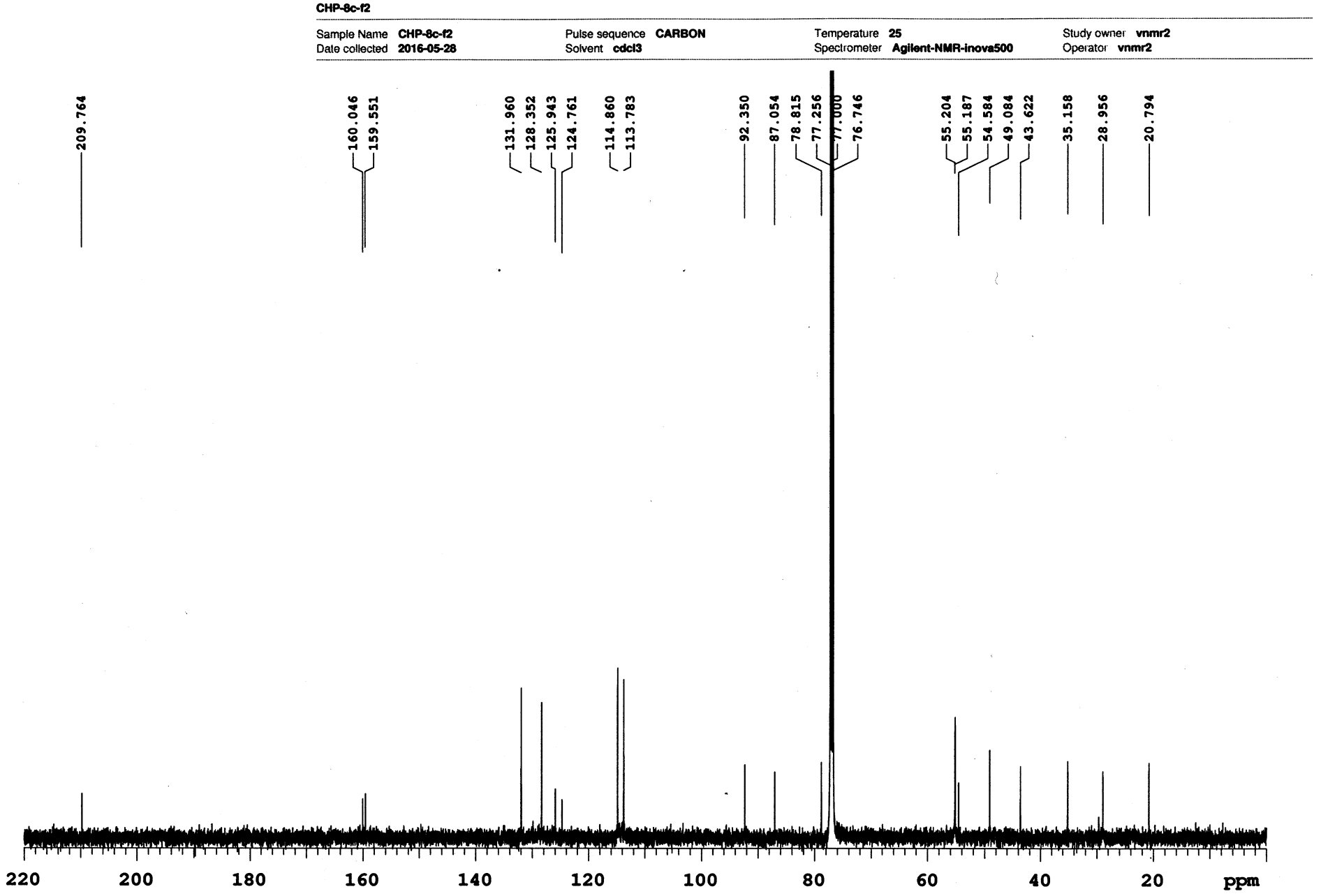
Fig S58. 1H NMR (CDCl3, 500 MHz) of compound 5c.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8c-f2/PROTON_05

Plot date 2016-05-31

Fig S59. 13C NMR (CDCl3, 125 MHz) of compound 5c.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8c-f2/CARBON_01

Plot date 2016-05-31

Fig S60. DEPT of compound 5c.

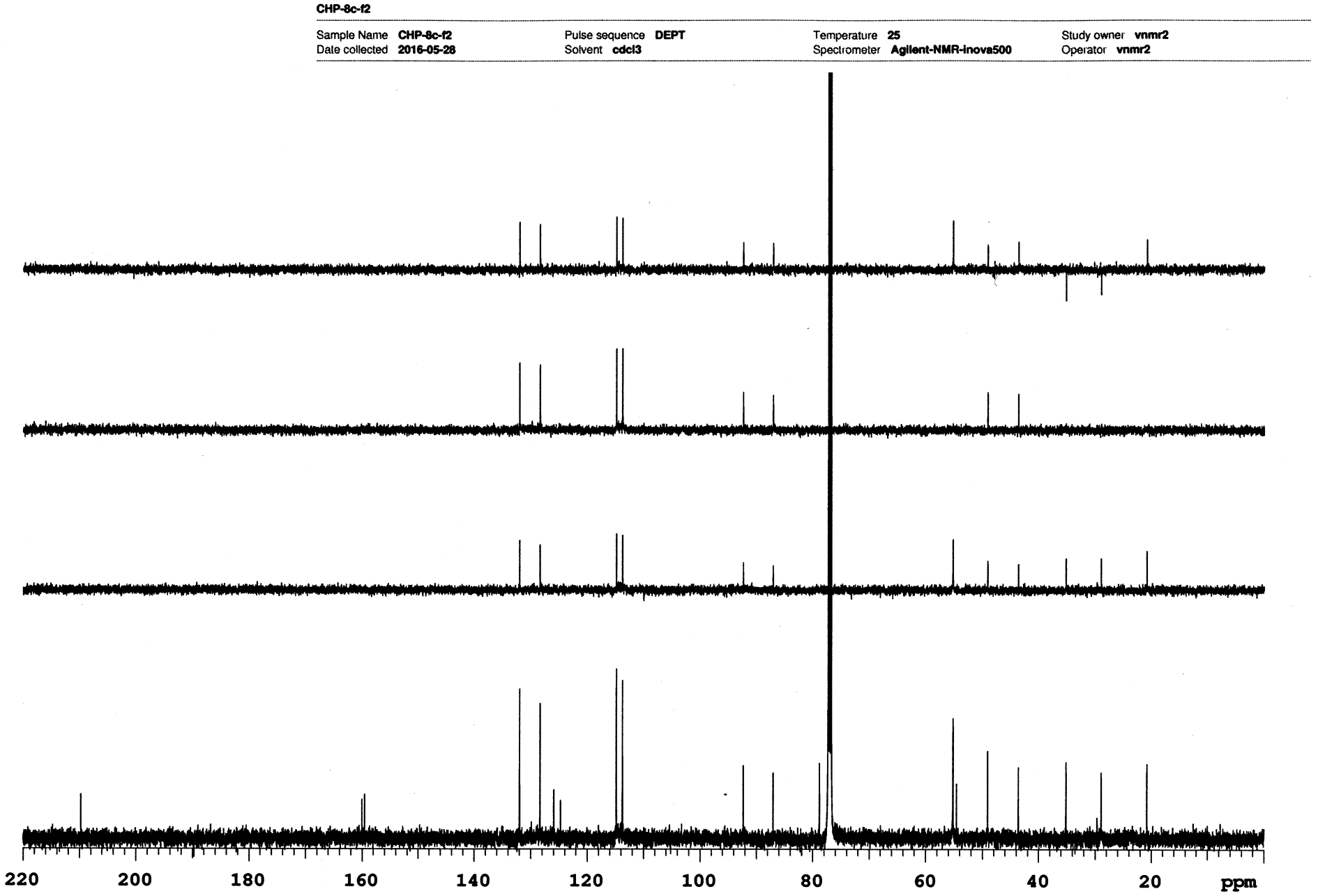
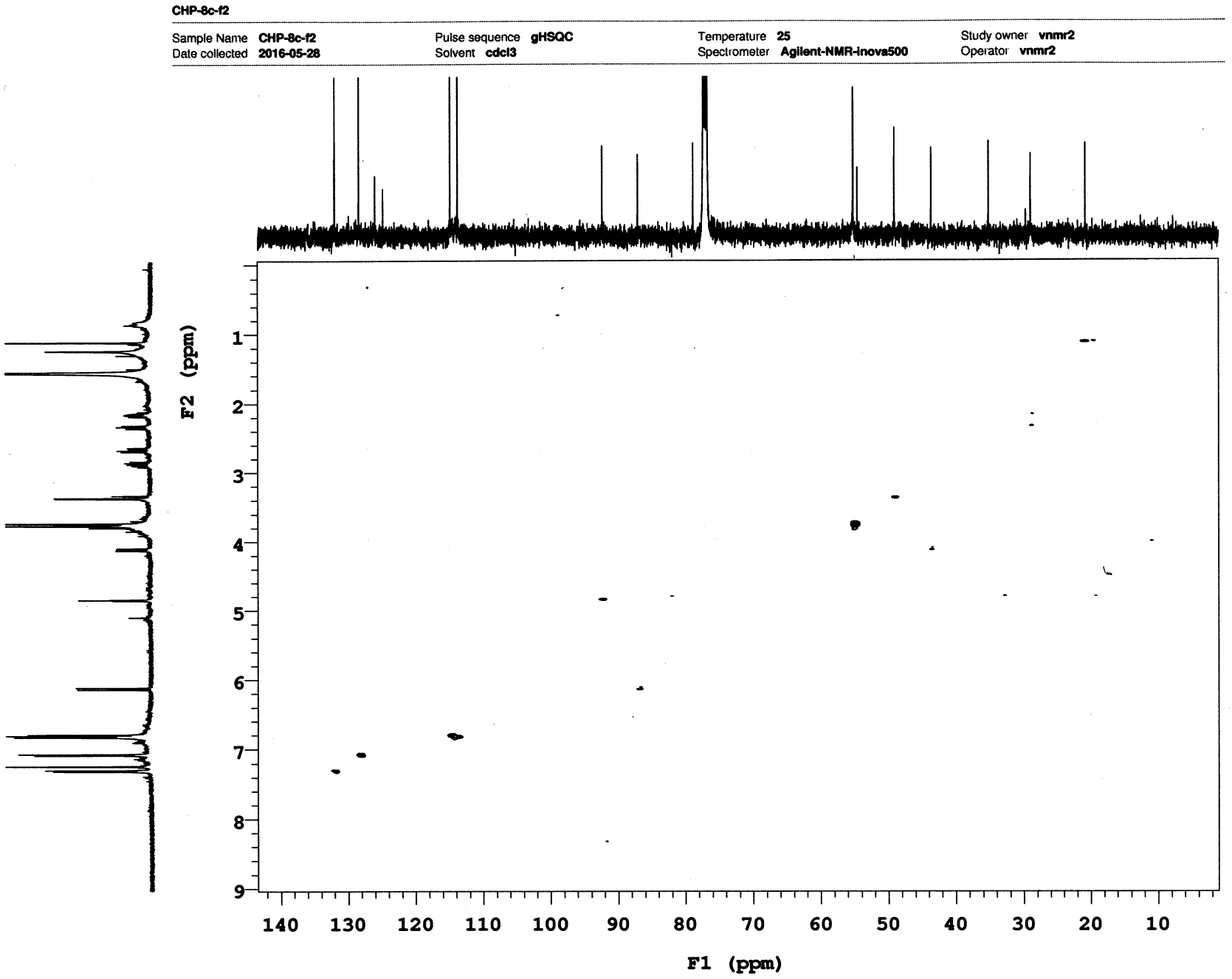


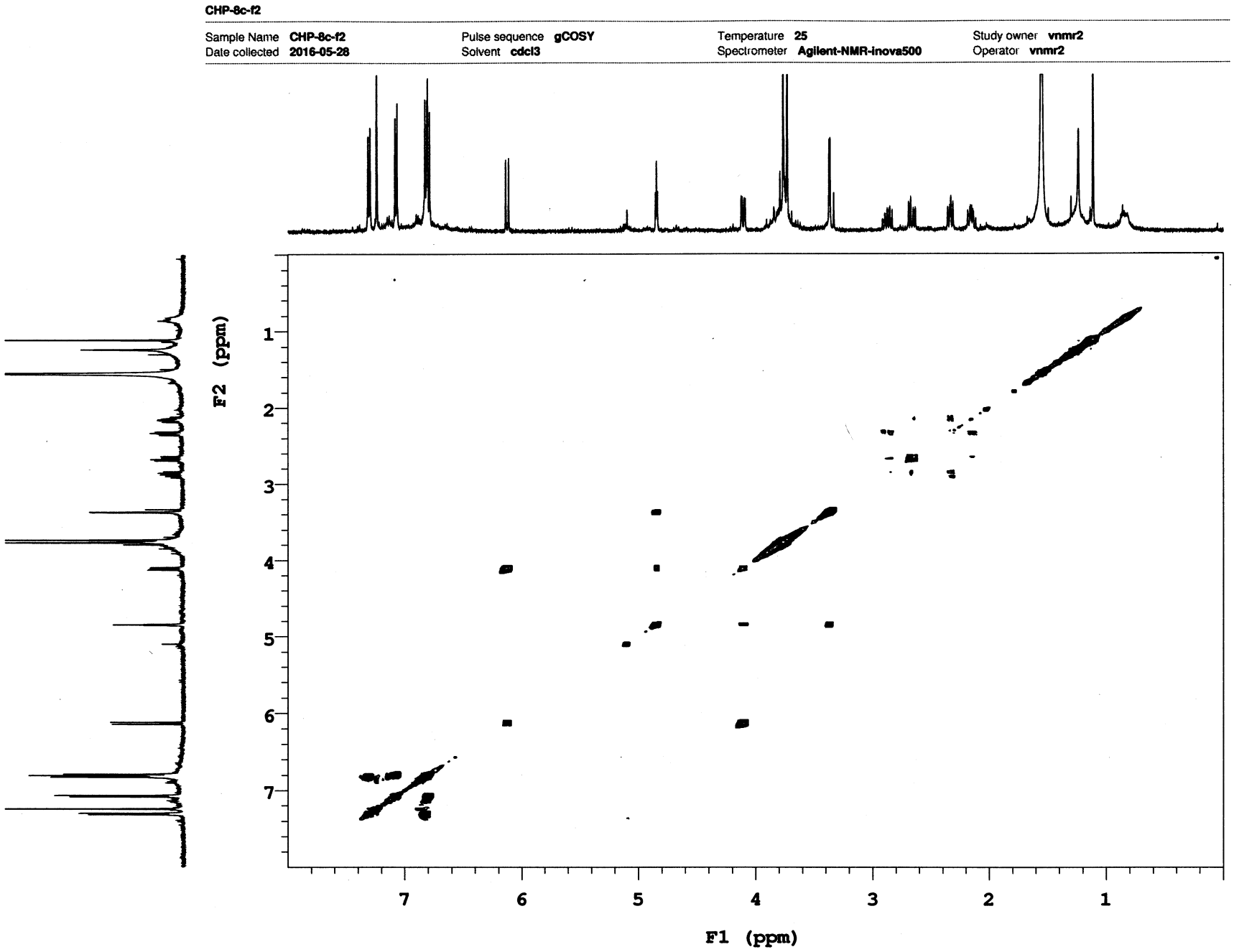
Fig S61. HSQC of compound 5c.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8c-f2/gHSQC_01

Plot date 2016-05-31

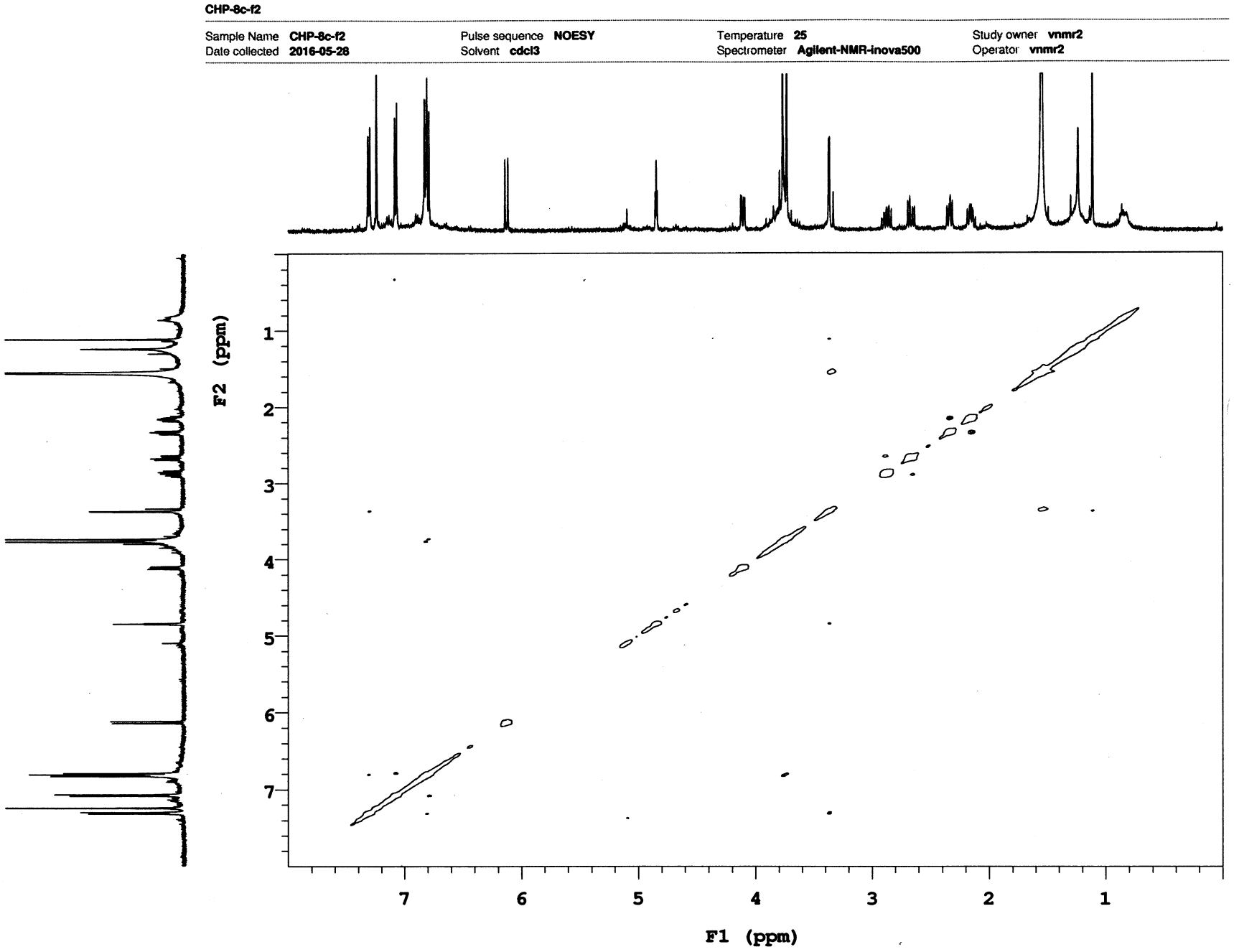
Fig S62. COSY of compound 5c.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8c-f2/gCOSY_01

Plot date 2016-05-31

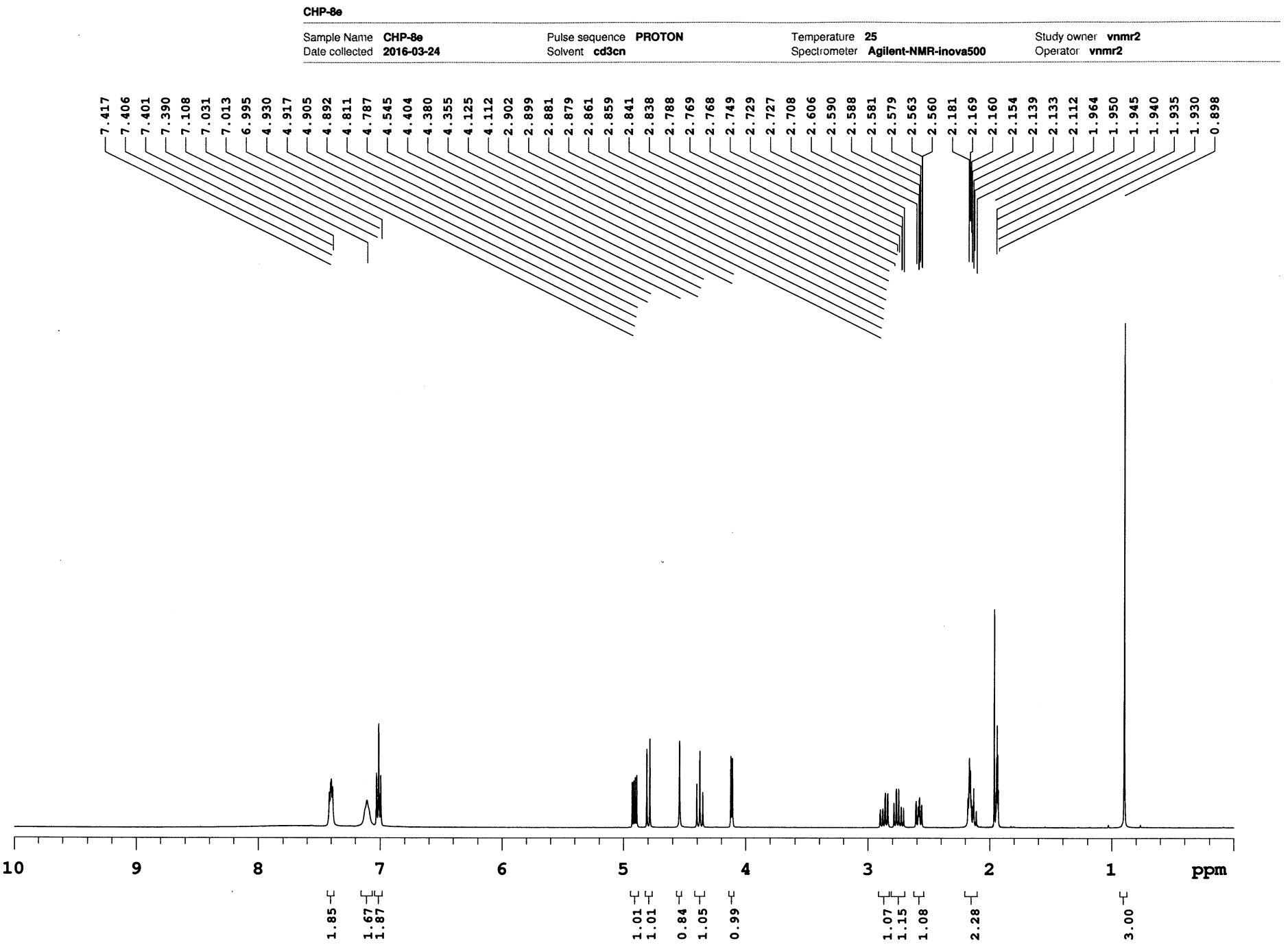
Fig S63. NOESY of compound 5c.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8c-f2/NOESY_01

Plot date 2016-05-31

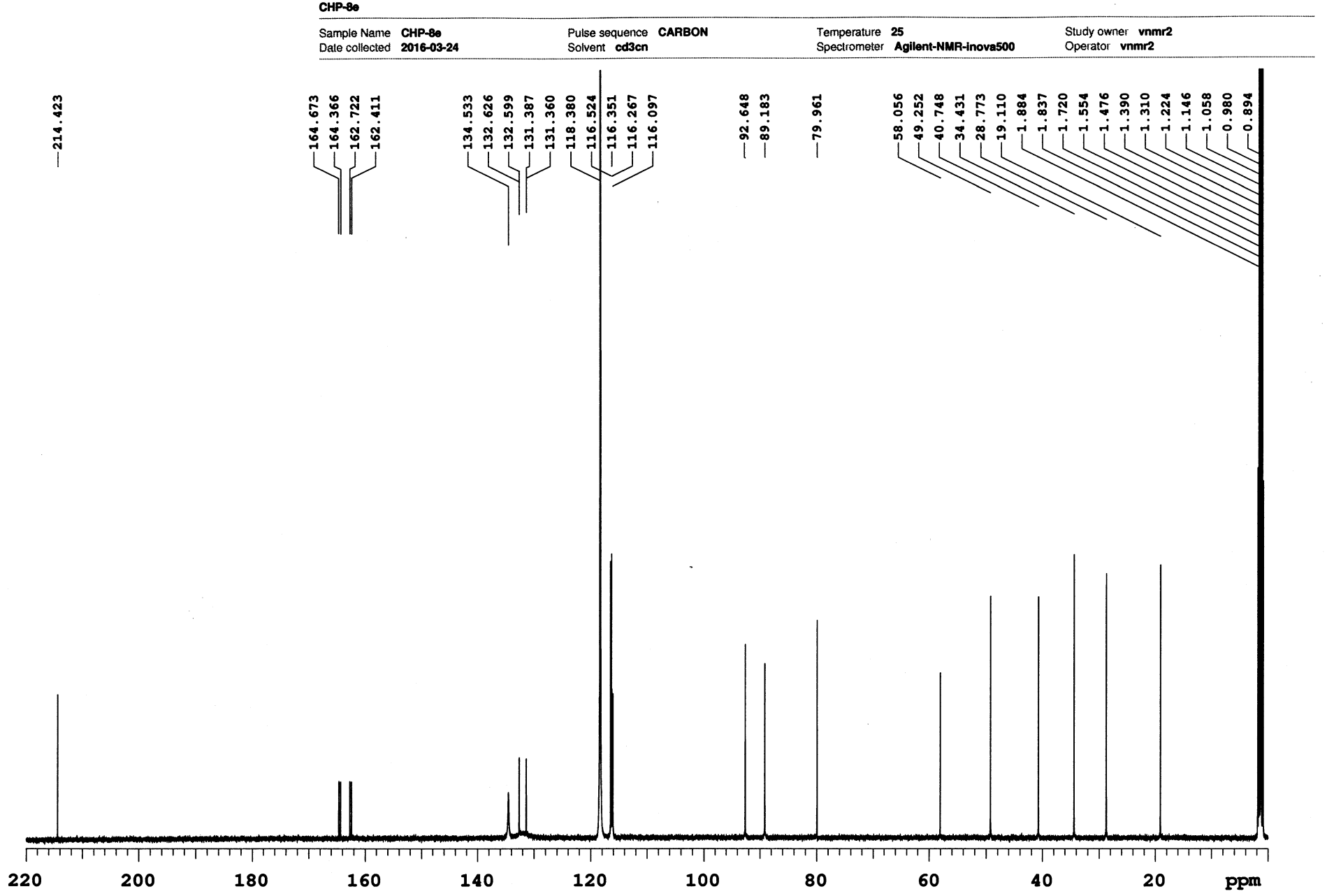
Fig S64. 1H NMR (CD3CN, 500 MHz) of compound 3d.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e/PROTON_08

Plot date 2016-03-29

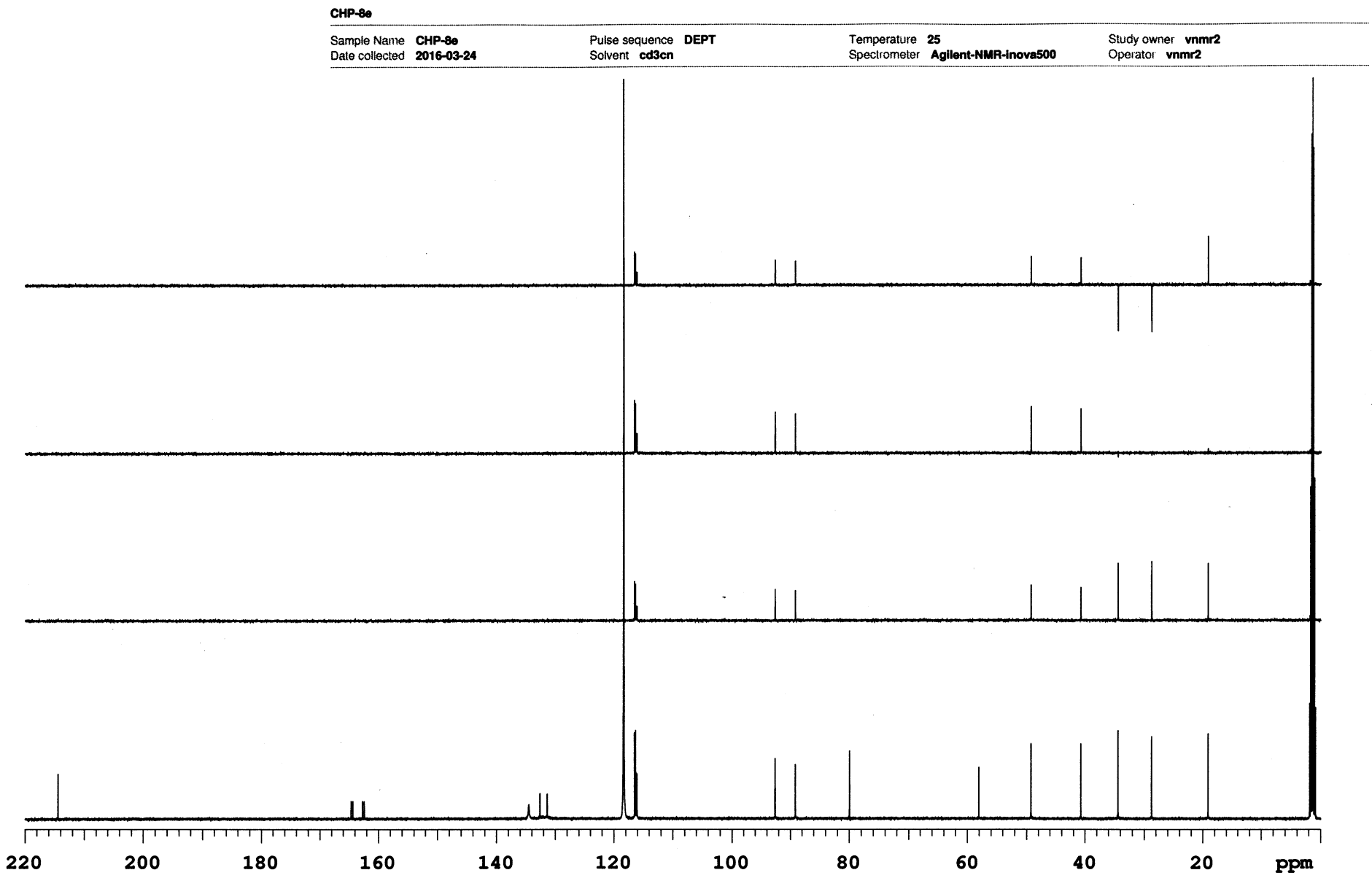
Fig S65. 13C NMR (CD3CN, 125 MHz) of compound 3d.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e/CARBON_03

Plot date 2016-03-29

Fig S66. DEPT of compound 3d.



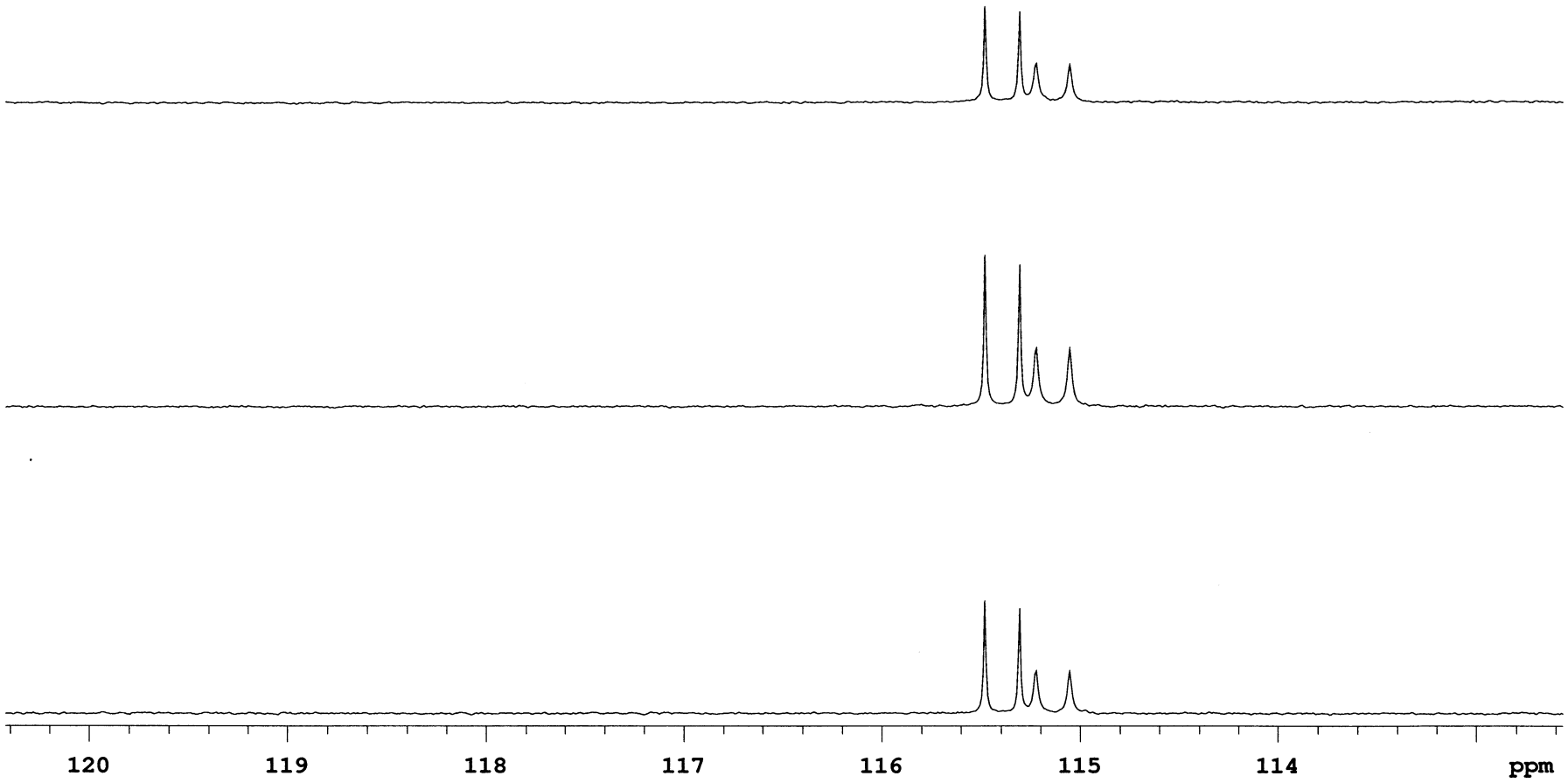
Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e/DEPT_02

Plot date 2016-03-29

Fig S67. DEPT of compound 3d, expanded.

CHP-8e

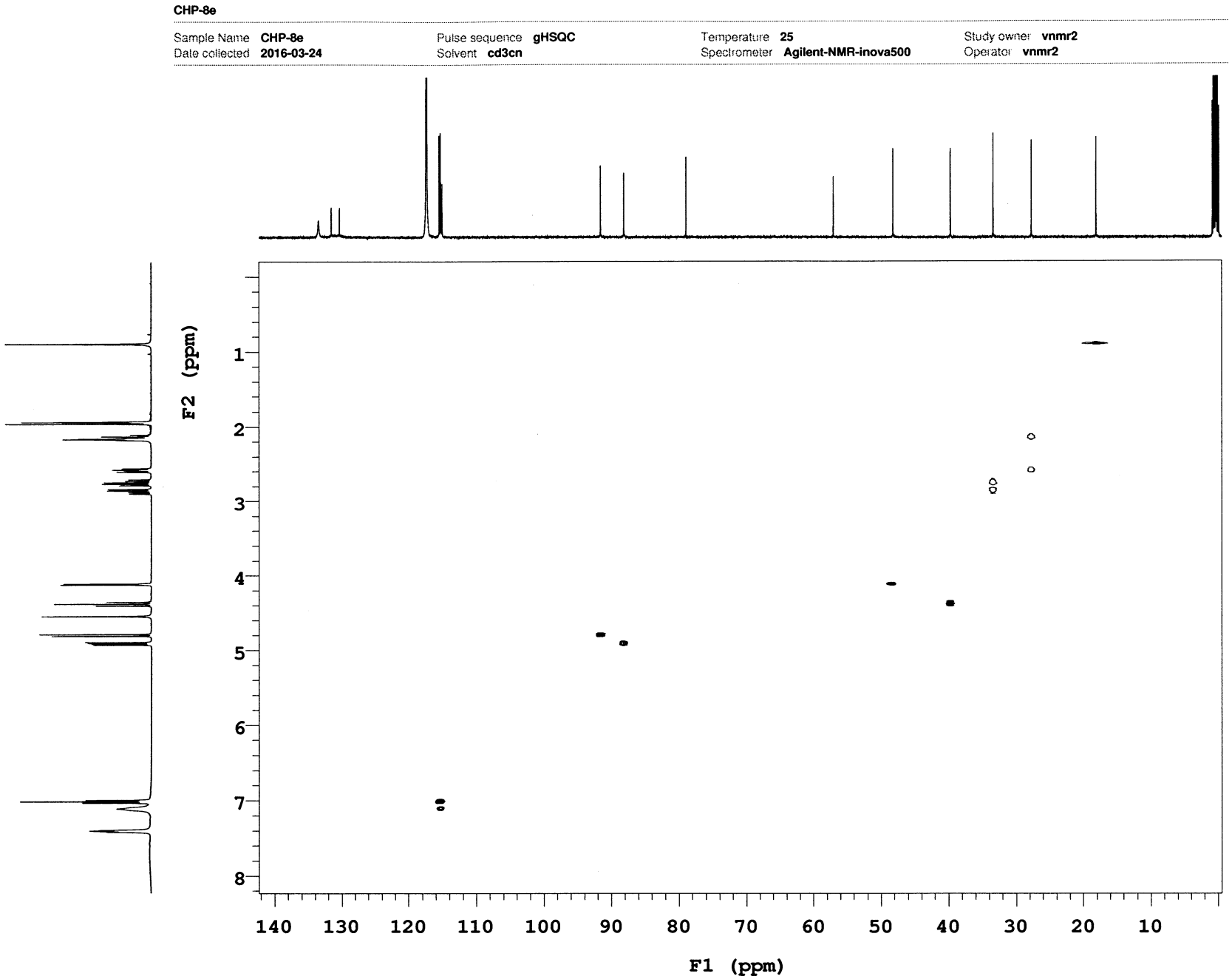
Sample Name **CHP-8e**	Pulse sequence **DEPT**	Temperature **25**	Study owner **vnmr2**
Date collected **2016-03-24**	Solvent **cd3cn**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e/DEPT_02.fid

Plot date 2016-05-04

Fig S68. HSQC of compound 3d.



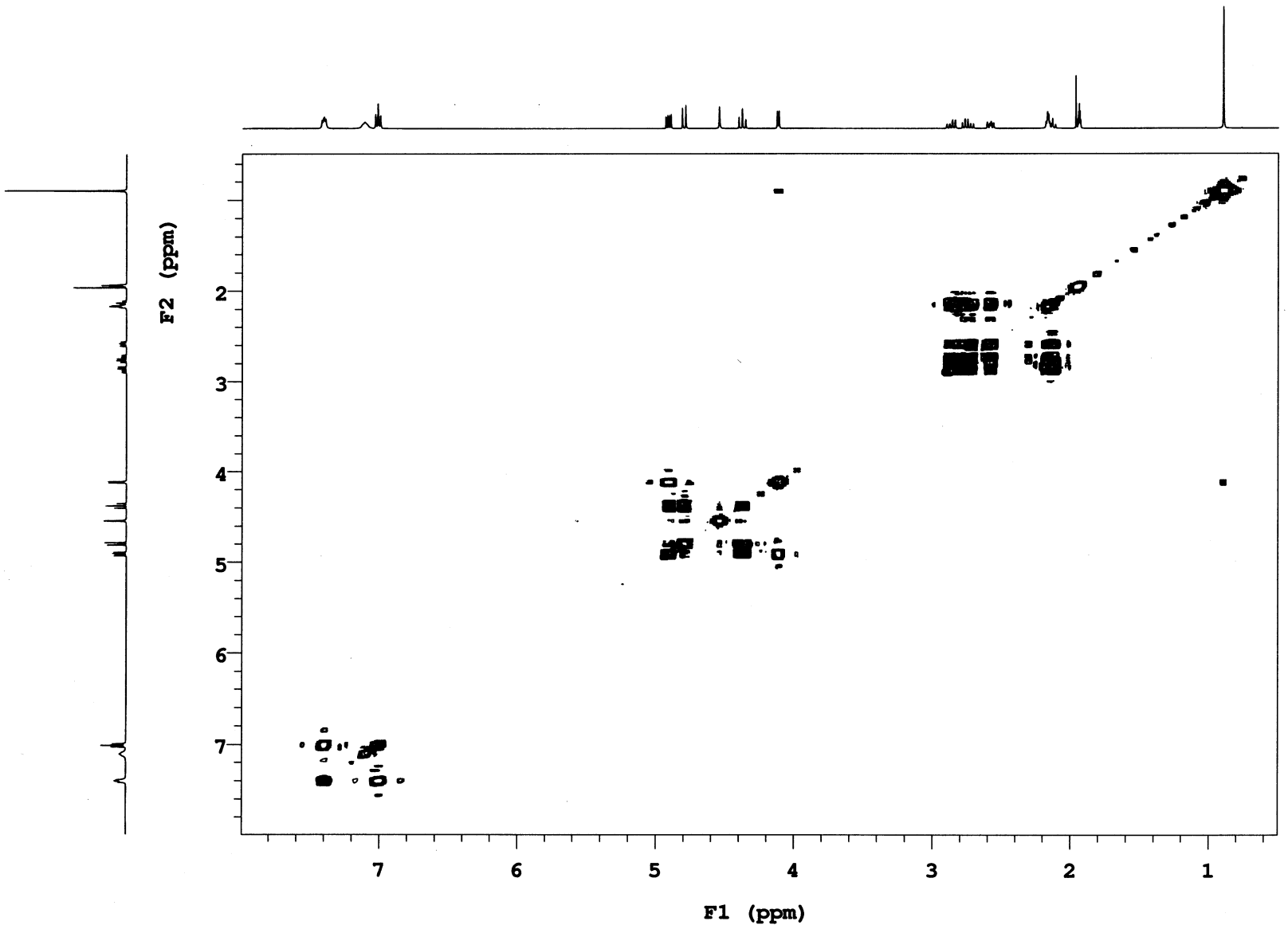
Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e/gHSQC_02.fid

Plot date 2016-04-22

Fig S69. COSY of compound 3d.

CHP-8e

Sample Name	**CHP-8e**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-03-24**	Solvent	**cd3cn**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



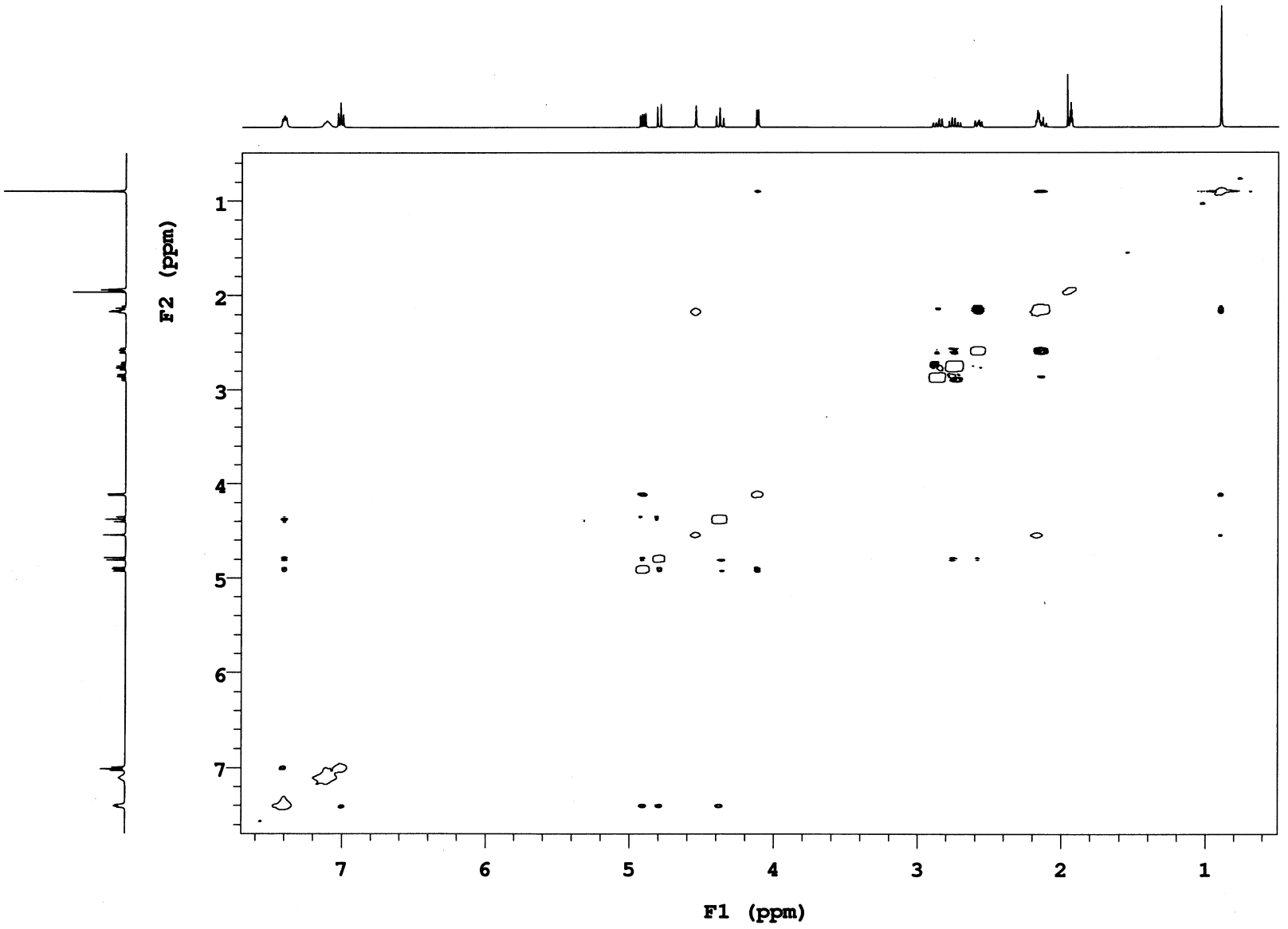
Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e/gCOSY_02

Plot date 2016-03-29

Fig S70. NOESY of compound 3d.

CHP-8e

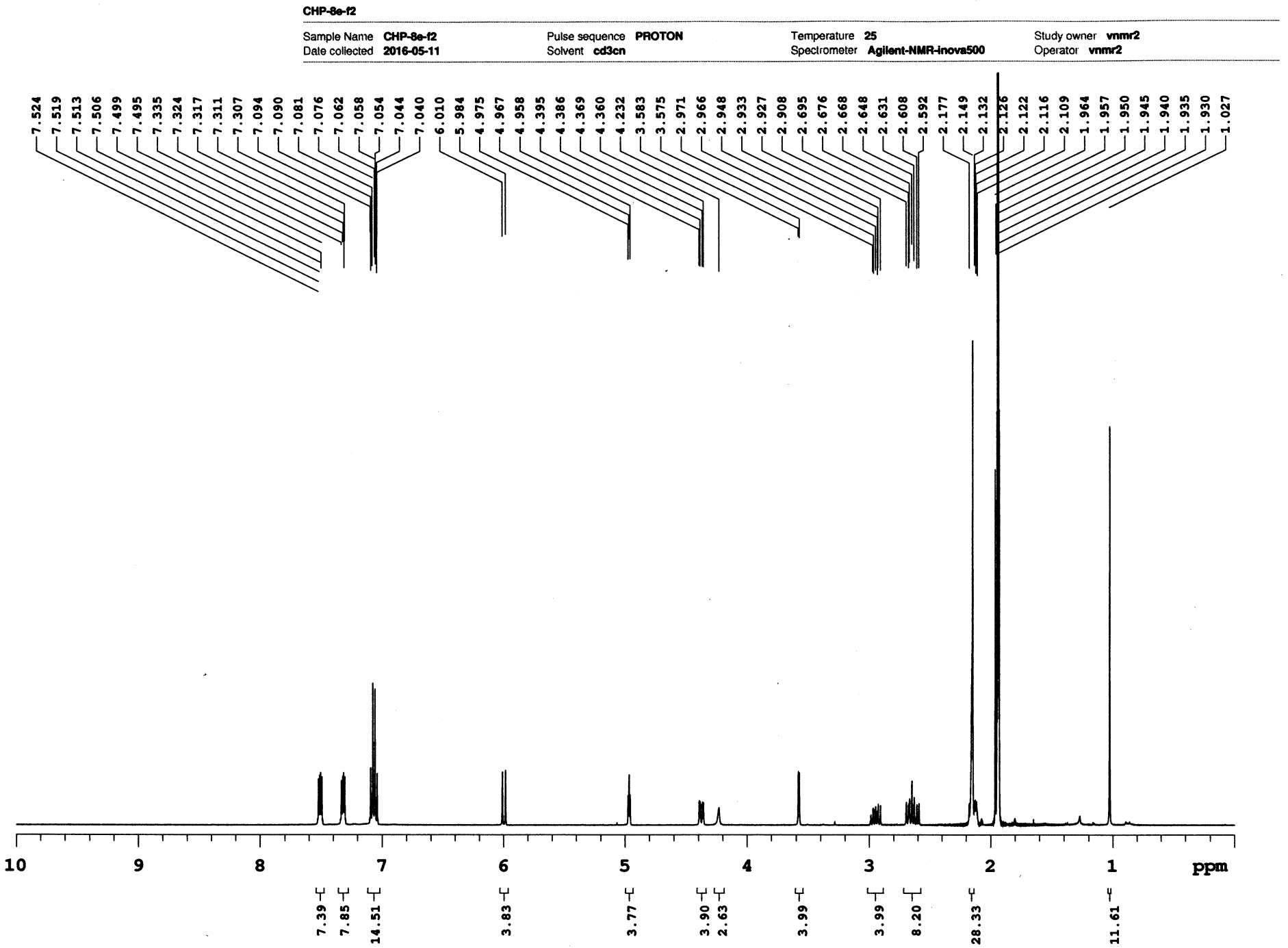
Sample Name **CHP-8e**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2016-03-24**	Solvent **cd3cn**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e/NOESY_02

Plot date 2016-03-29

Fig S71. 1H NMR (CD3CN, 500 MHz) of compound 5d.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e-f2/PROTON_04

Plot date 2016-05-12

Fig S72. 13C NMR (CD3CN, 125 MHz) of compound 5d.

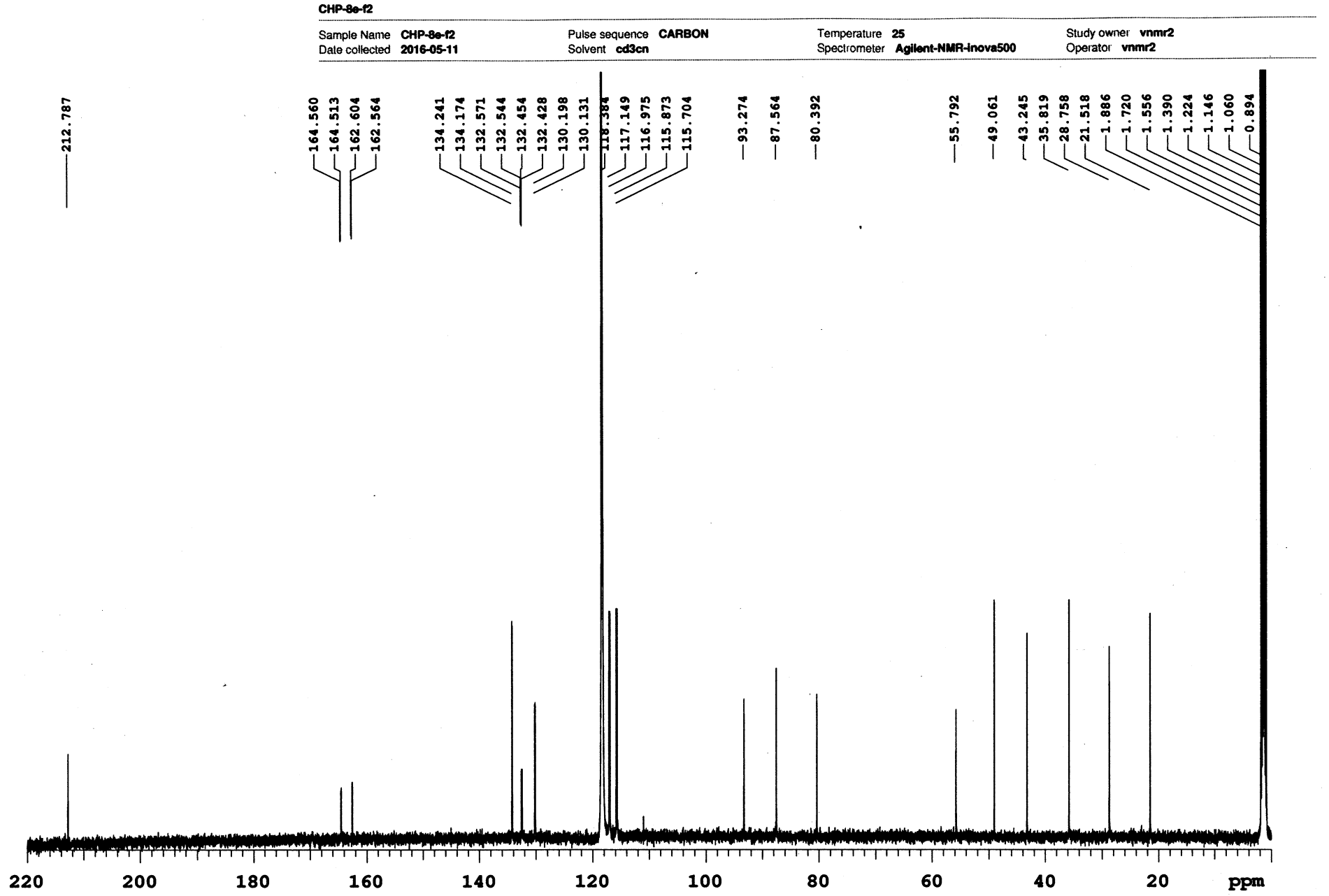
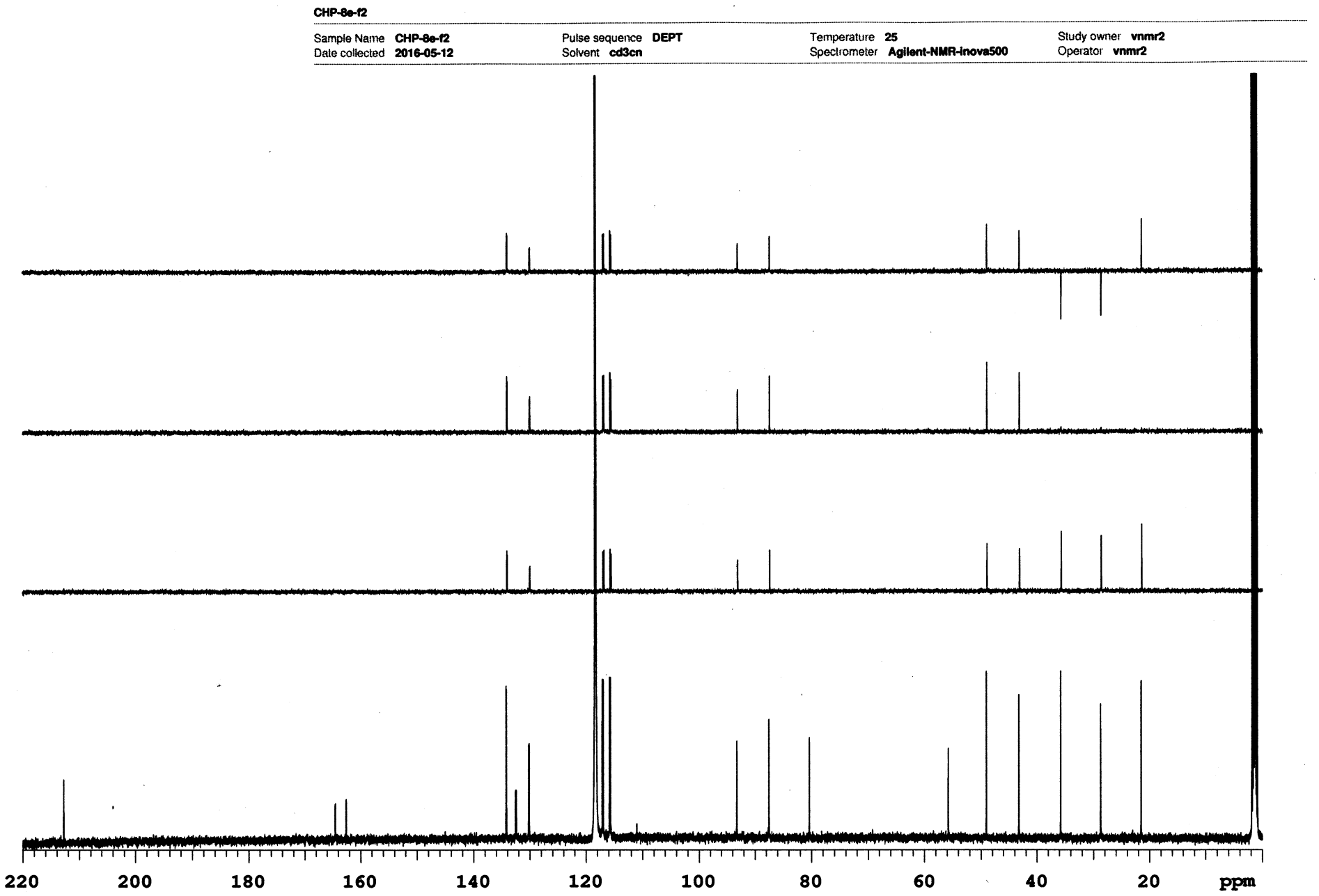


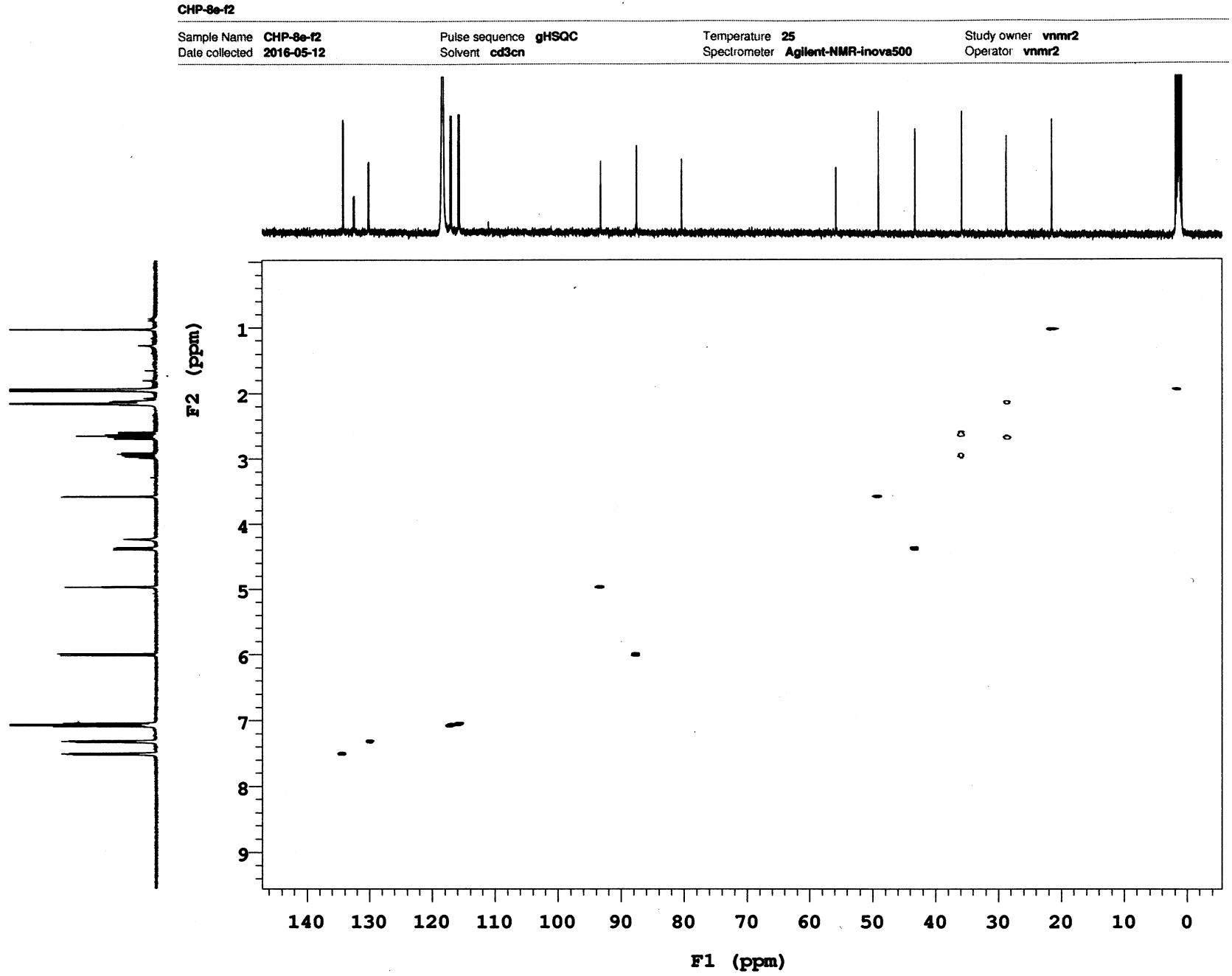
Fig S73. DEPT of compound 5d.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e-f2/DEPT_01

Plot date 2016-05-12

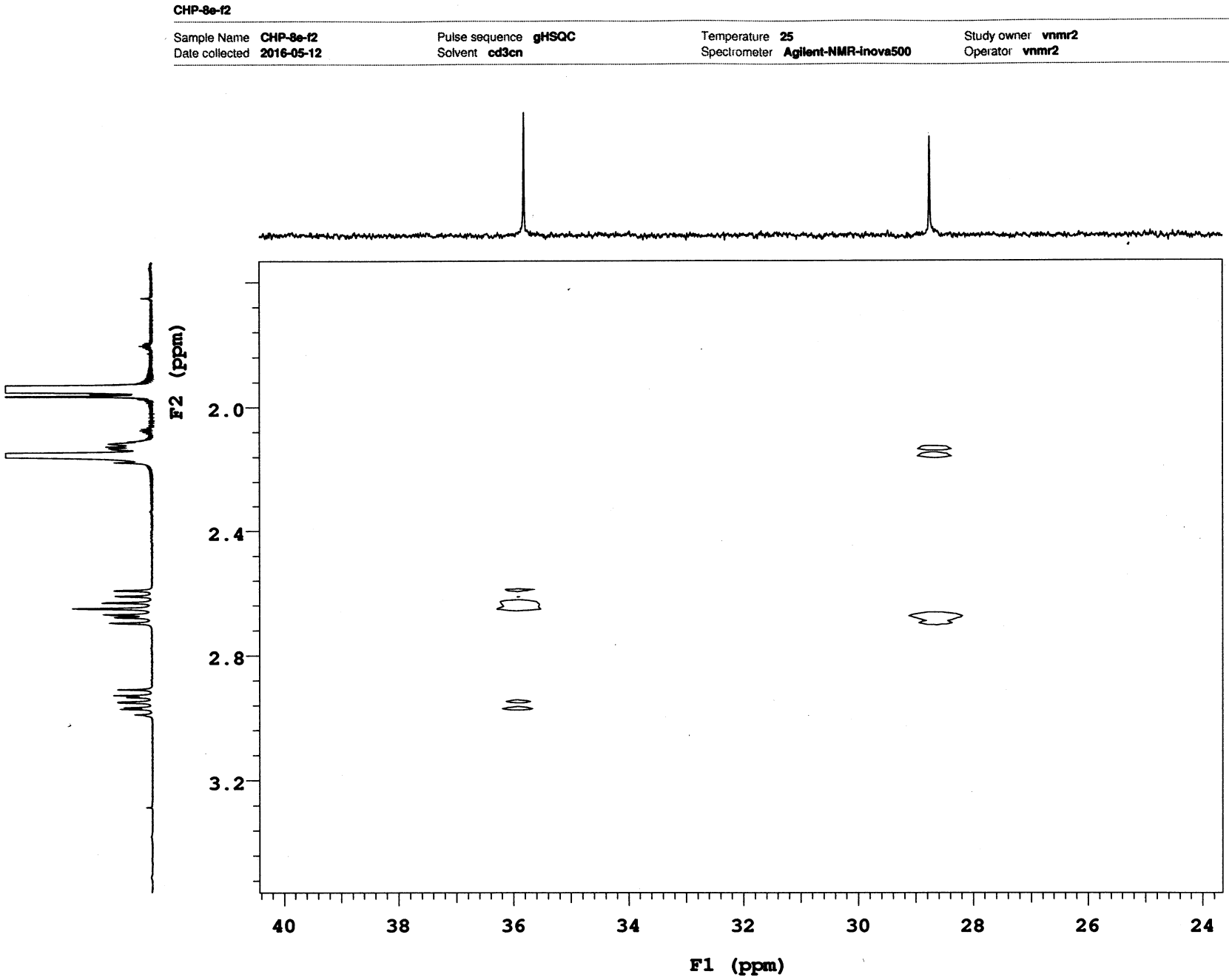
Fig S74. HSQC of compound 5d.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e-f2/gHSQC_01

Plot date 2016-05-12

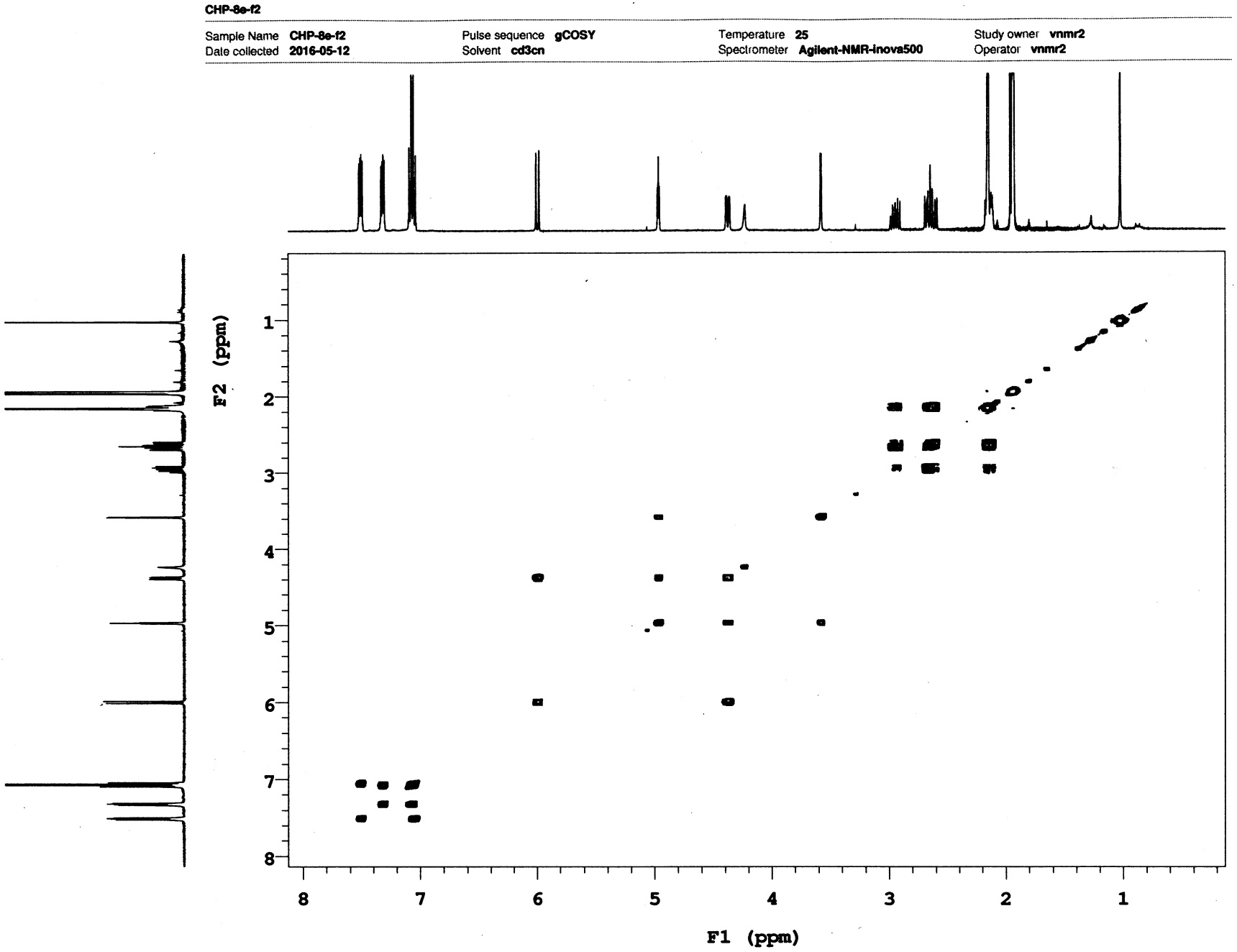
Fig S75. HSQC of compound 5d, expanded.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e-f2/gHSQC_01

Plot date 2016-05-12

Fig S76. COSY of compound 5d.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8e-f2/gCOSY_01

Plot date 2016-05-12

Fig S77. NOESY of compound 5d.

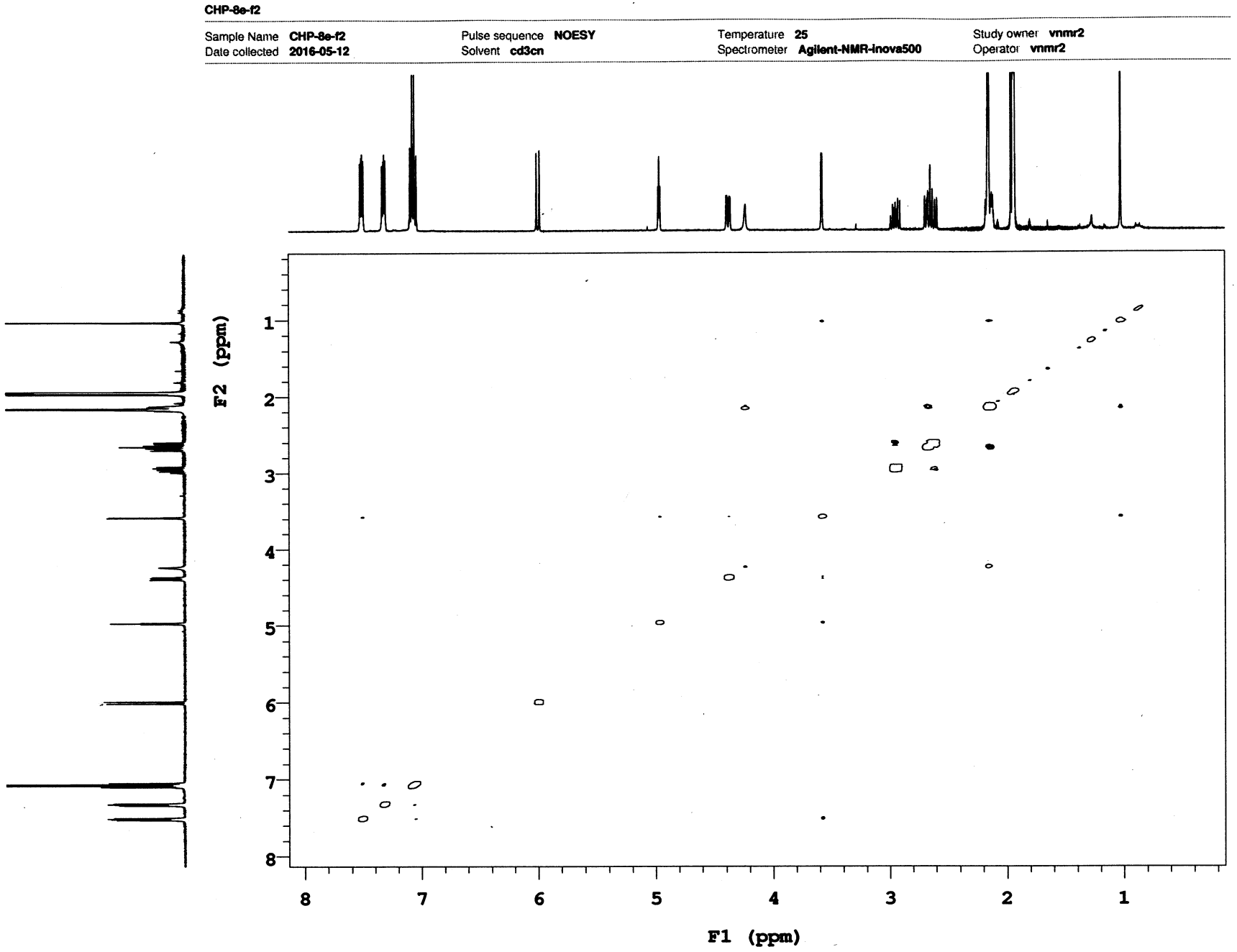
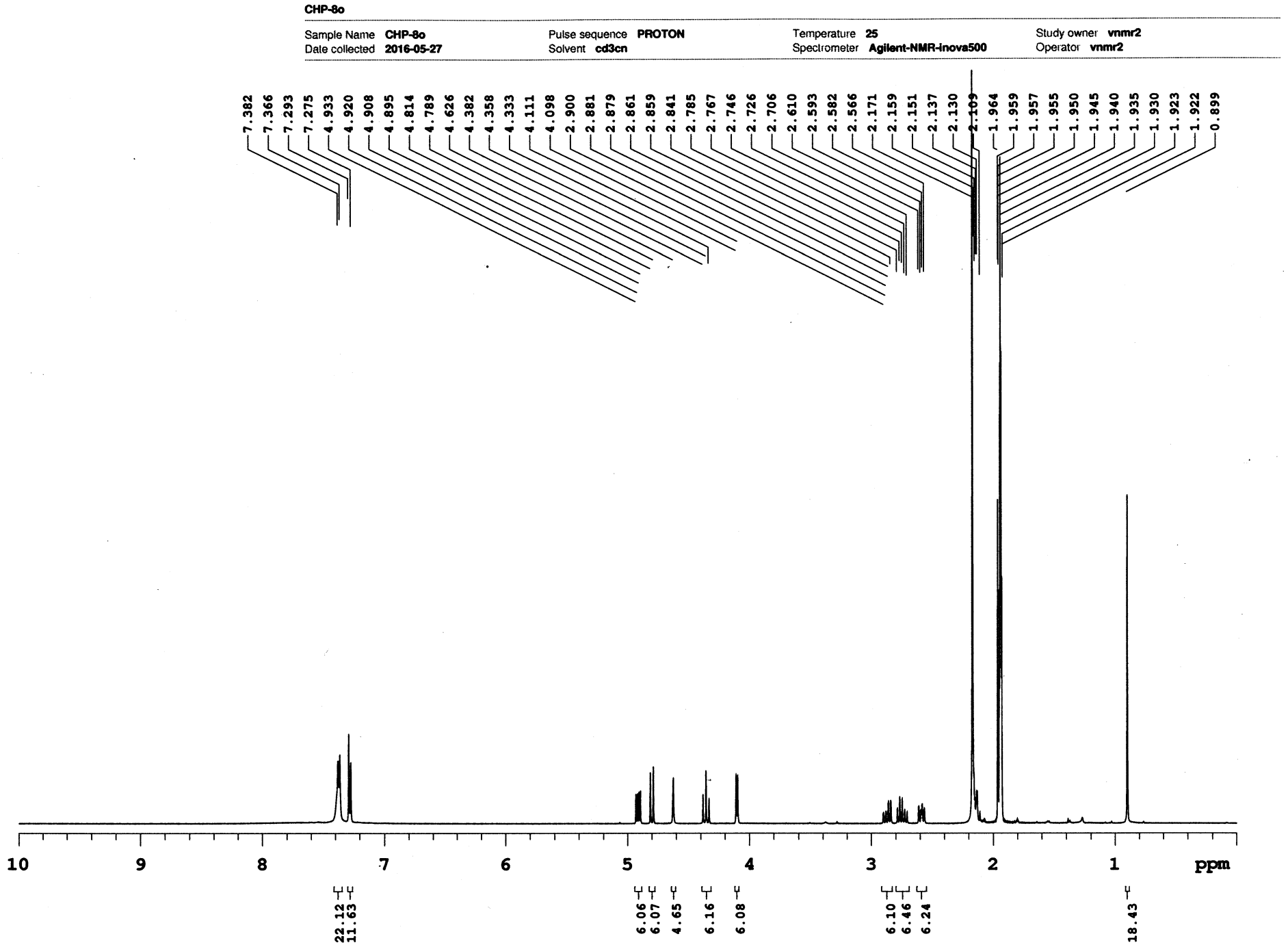


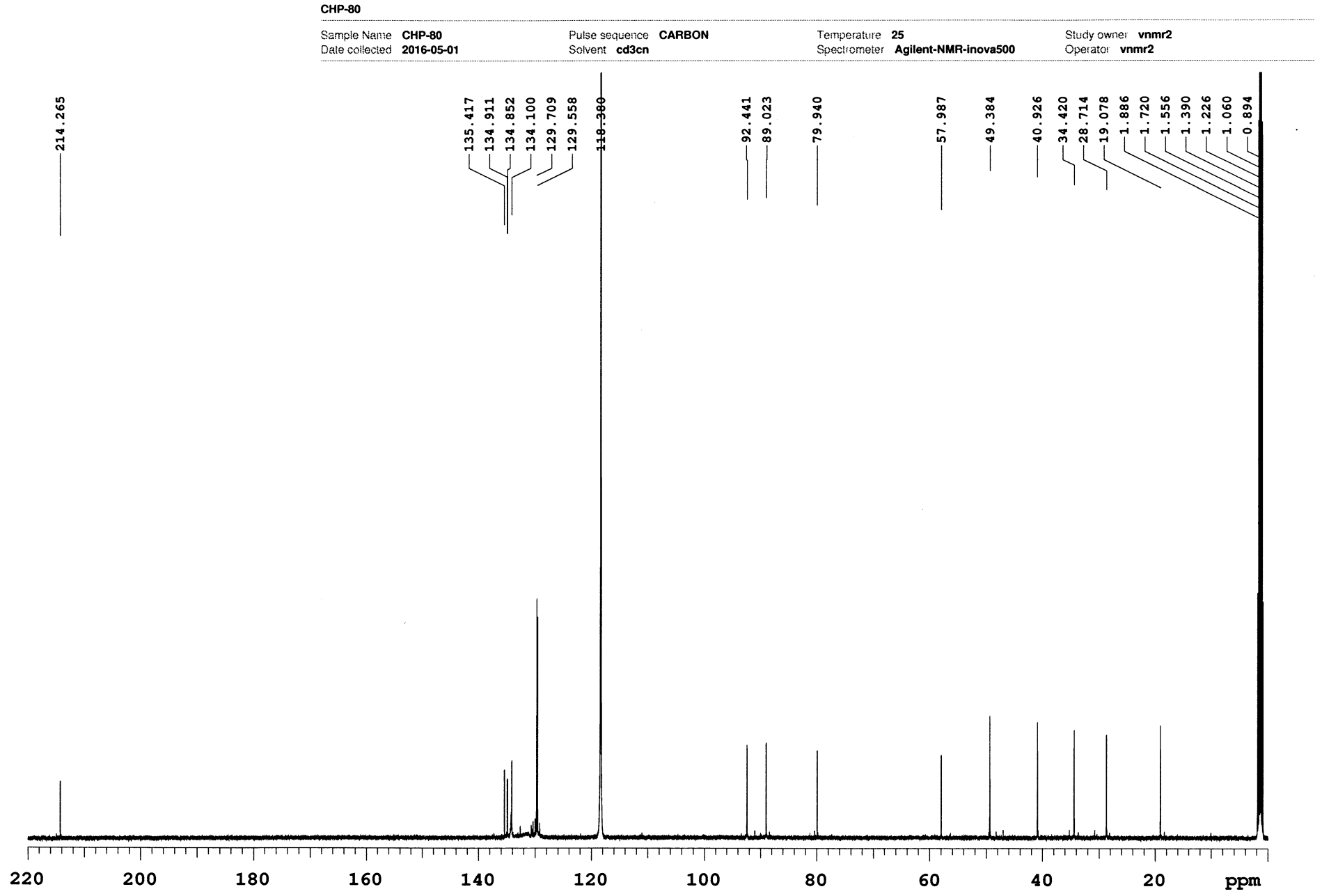
Fig S78. 1H NMR (CD3CN, 500 MHz) of compound 3e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8o/PROTON_02

Plot date 2016-05-27

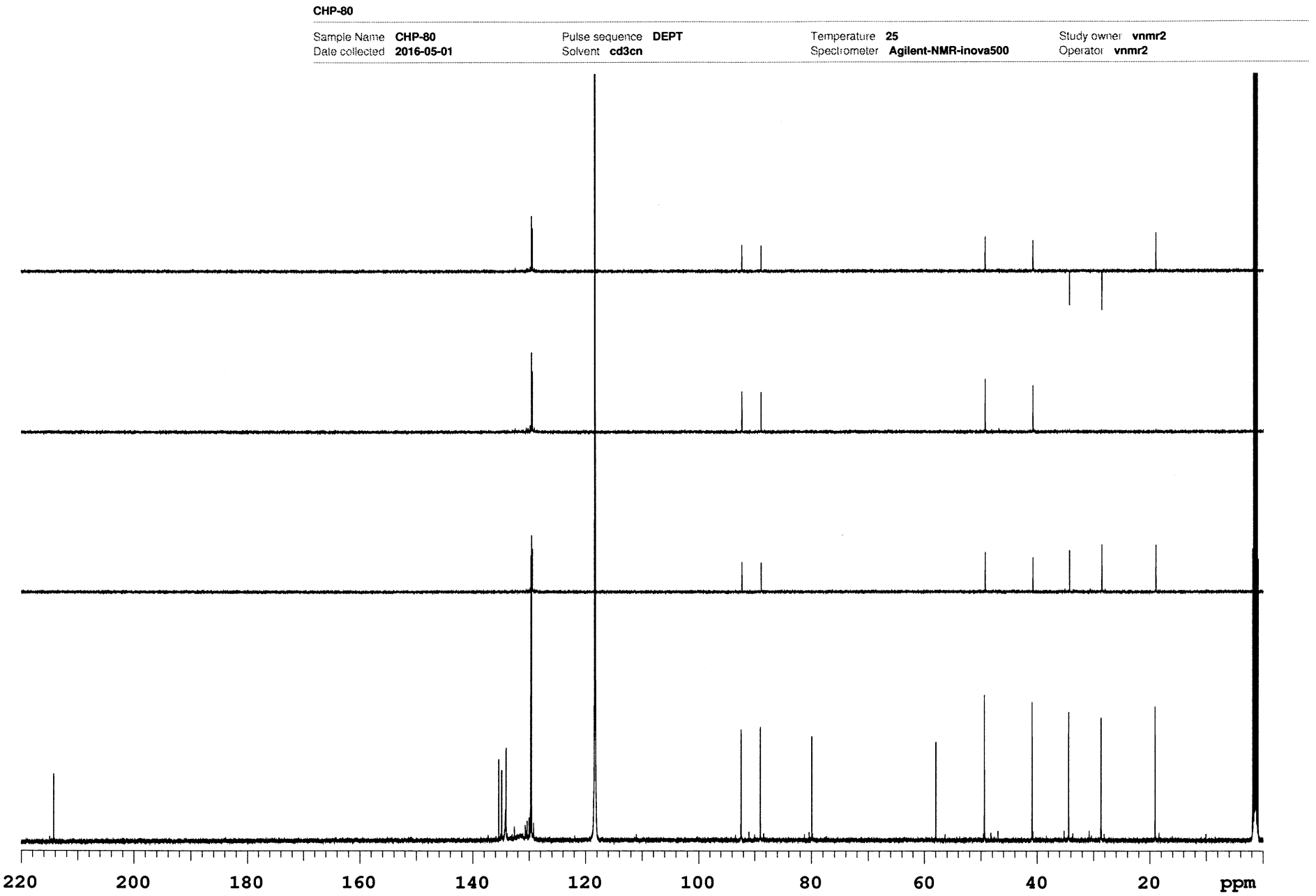
Fig S79. 13C NMR (CD3CN, 125 MHz) of compound 3e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-80/CARBON_01

Plot date 2016-05-02

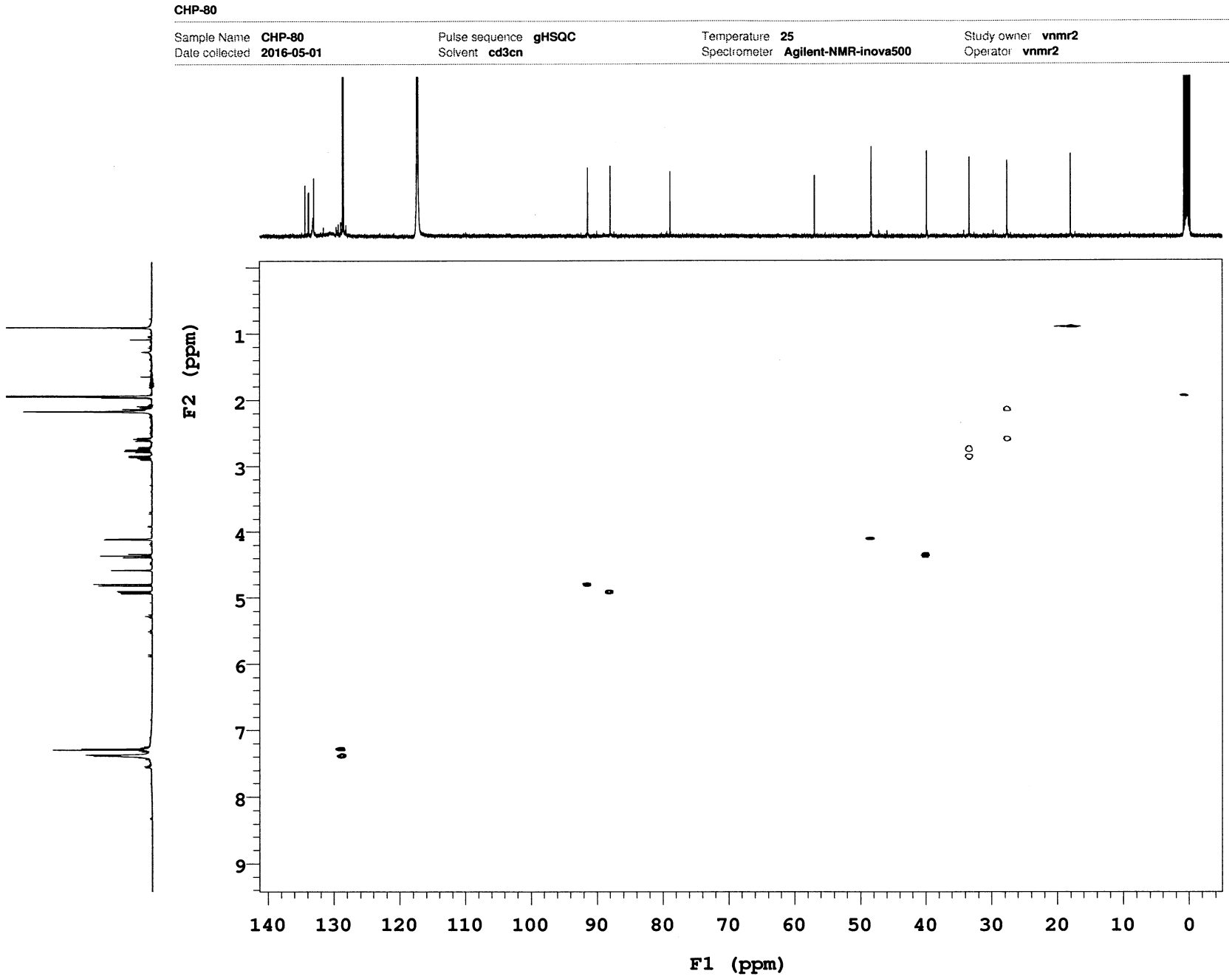
Fig S80. DEPT of compound 3e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-80/DEPT_01.fid

Plot date 2016-05-02

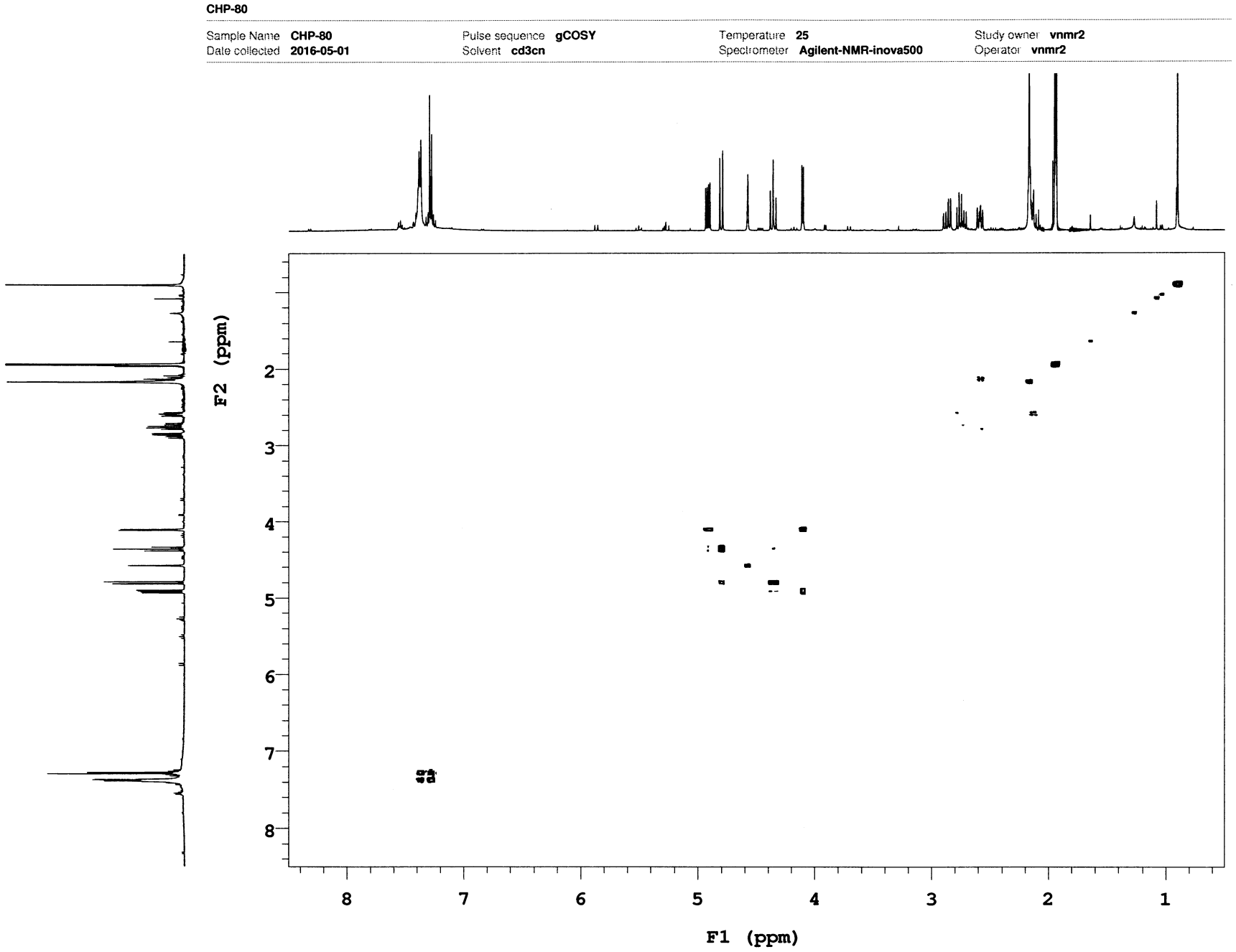
Fig S81. HSQC of compound 3e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-80/gHSQC_01

Plot date 2016-05-02

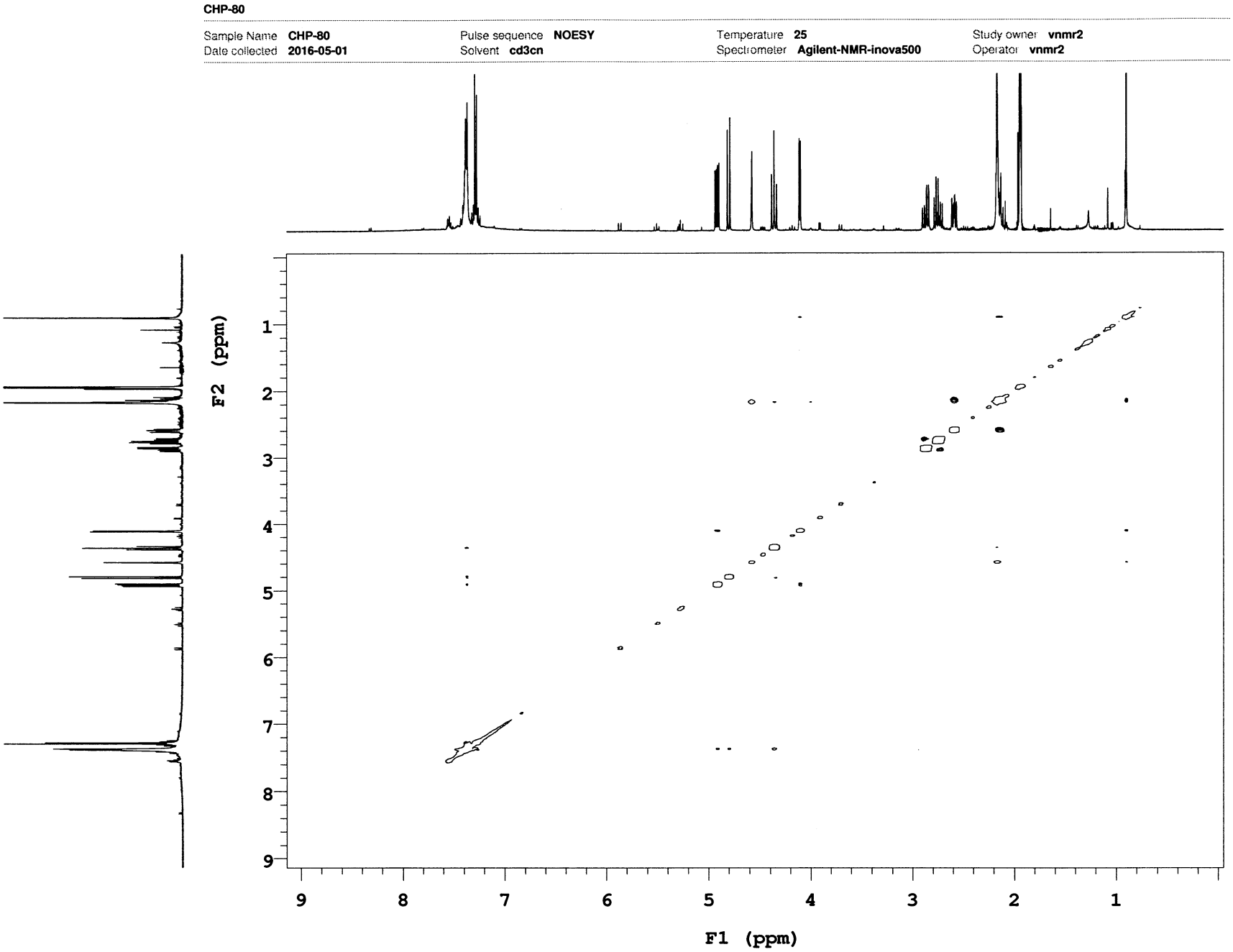
Fig S82. COSY of compound 3e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-80/gCOSY_01

Plot date 2016-05-02

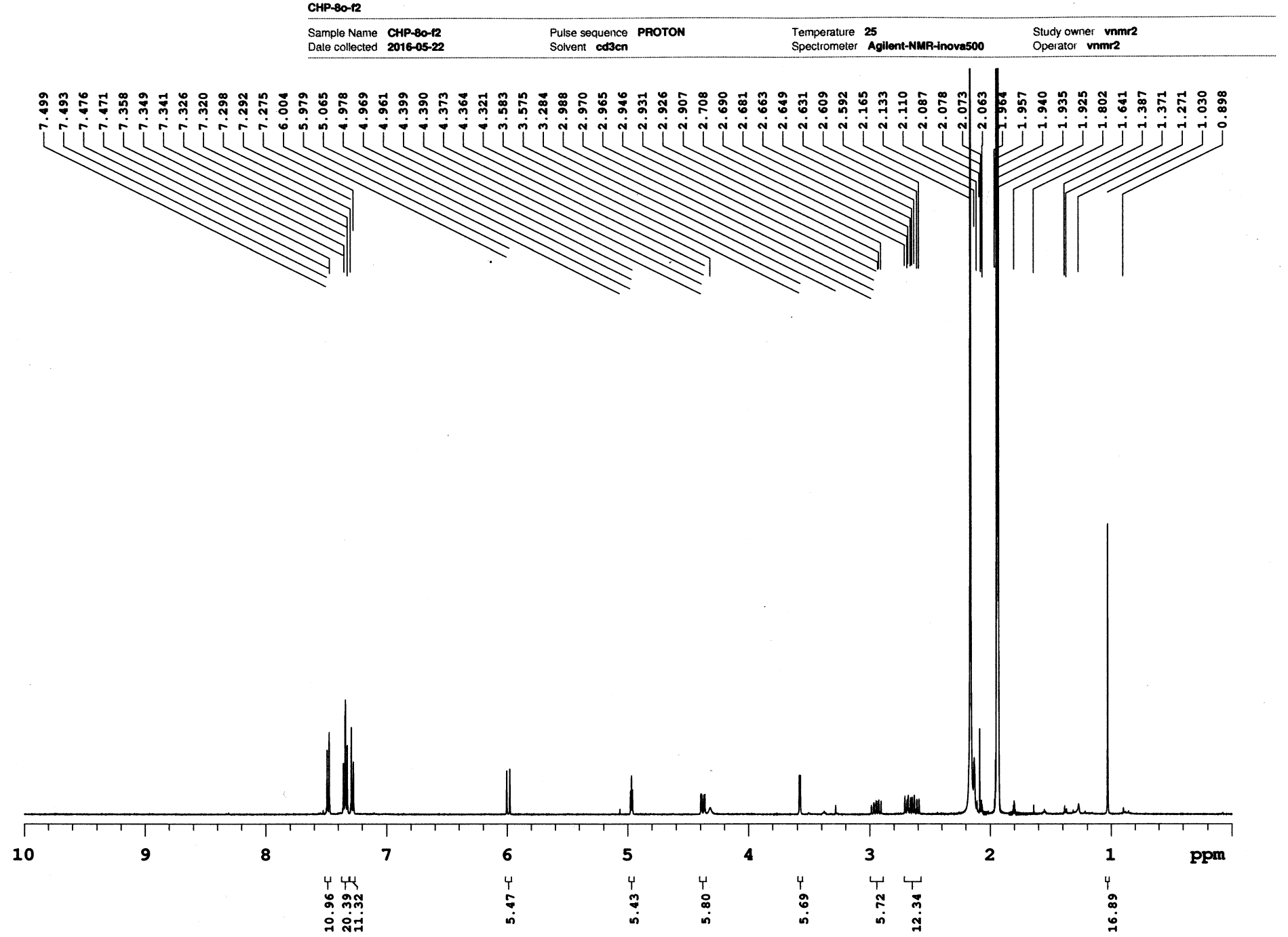
Fig S83. NOESY of compound 3e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-80/NOESY_01.fid

Plot date 2016-05-02

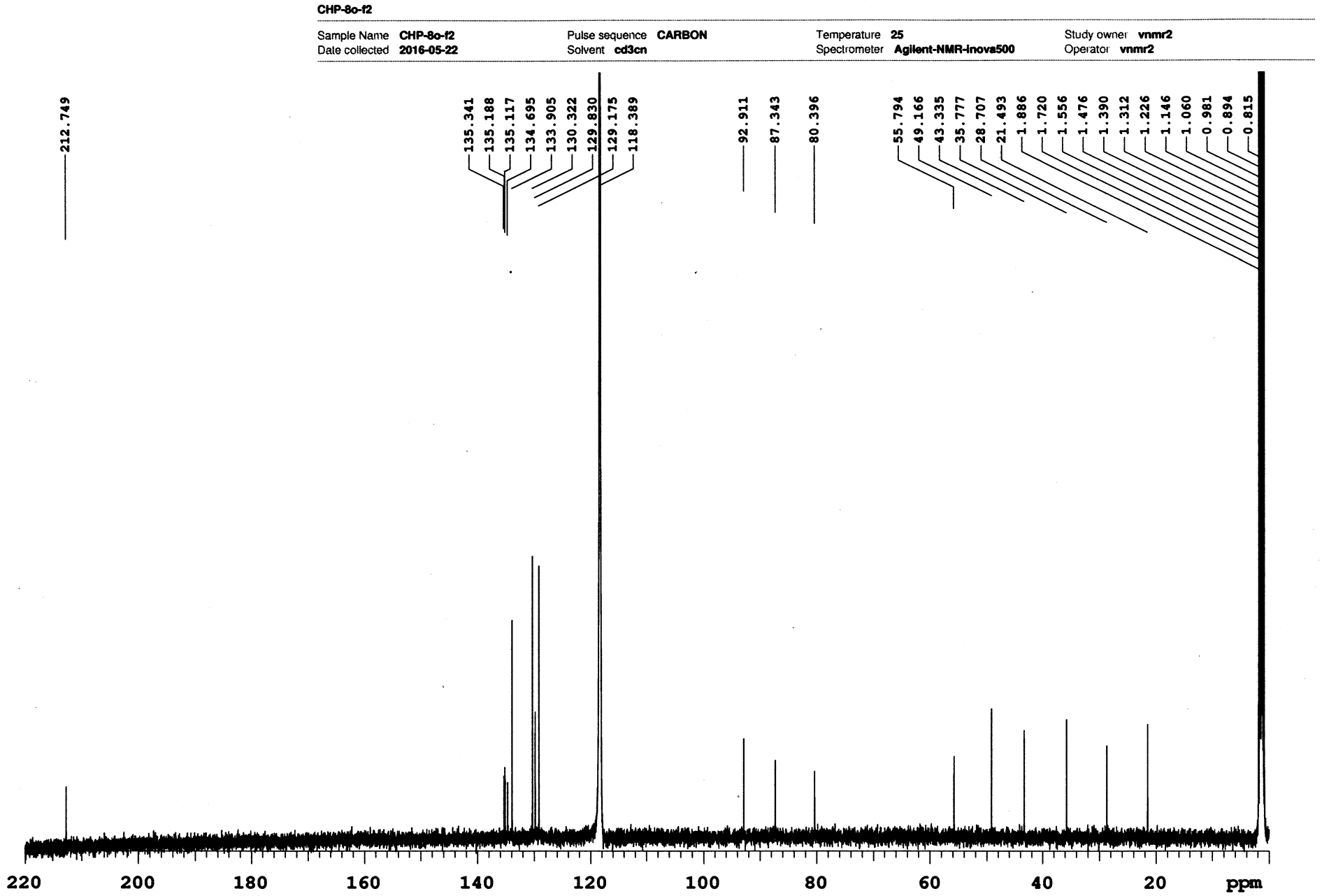
Fig S84. 1H NMR (CD3CN, 500 MHz) of compound 5e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8o-f2/PROTON_05

Plot date 2016-05-27

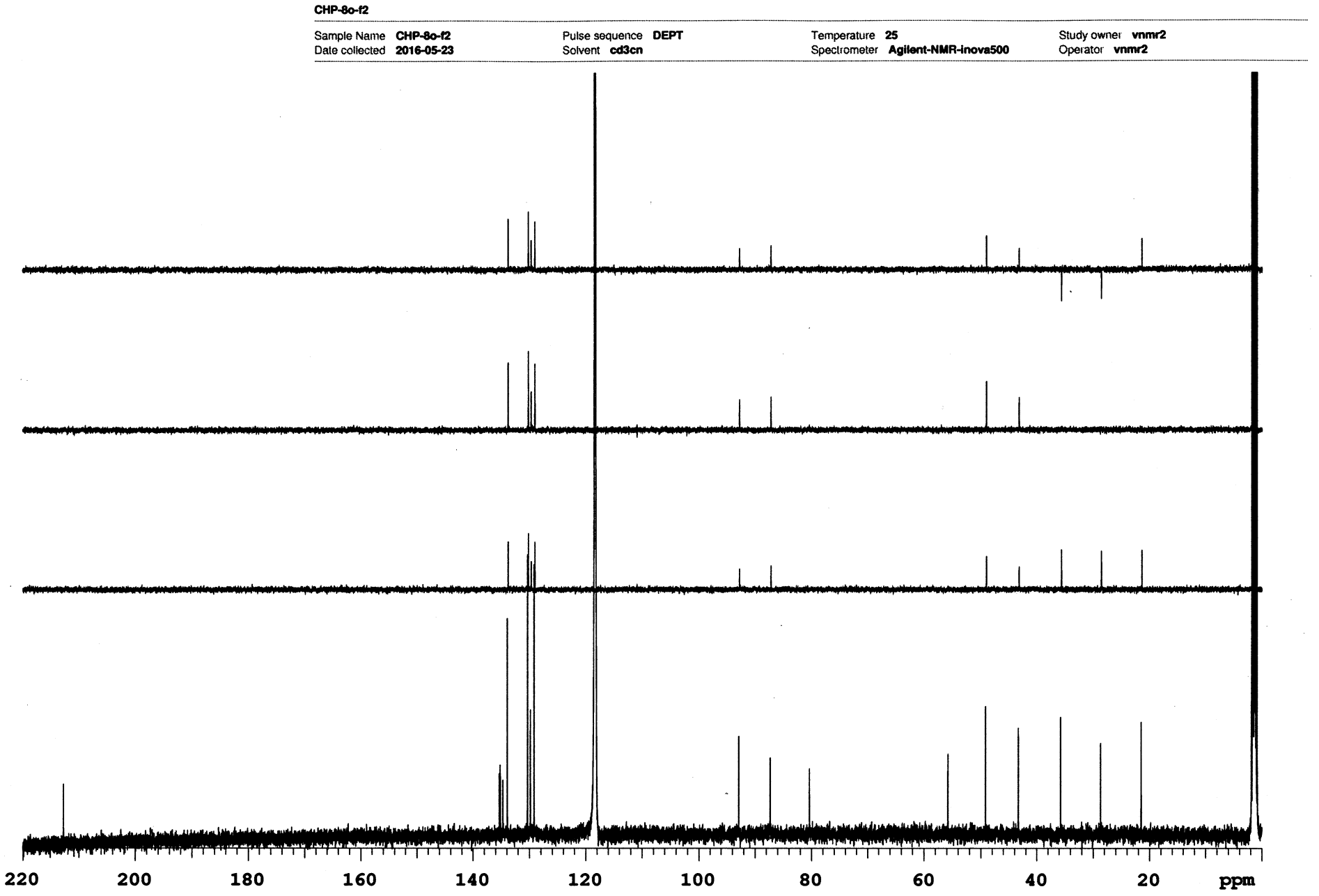
Fig S85. 13C NMR (CD3CN, 125 MHz) of compound 5e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8o-f2/CARBON_01

Plot date 2016-05-27

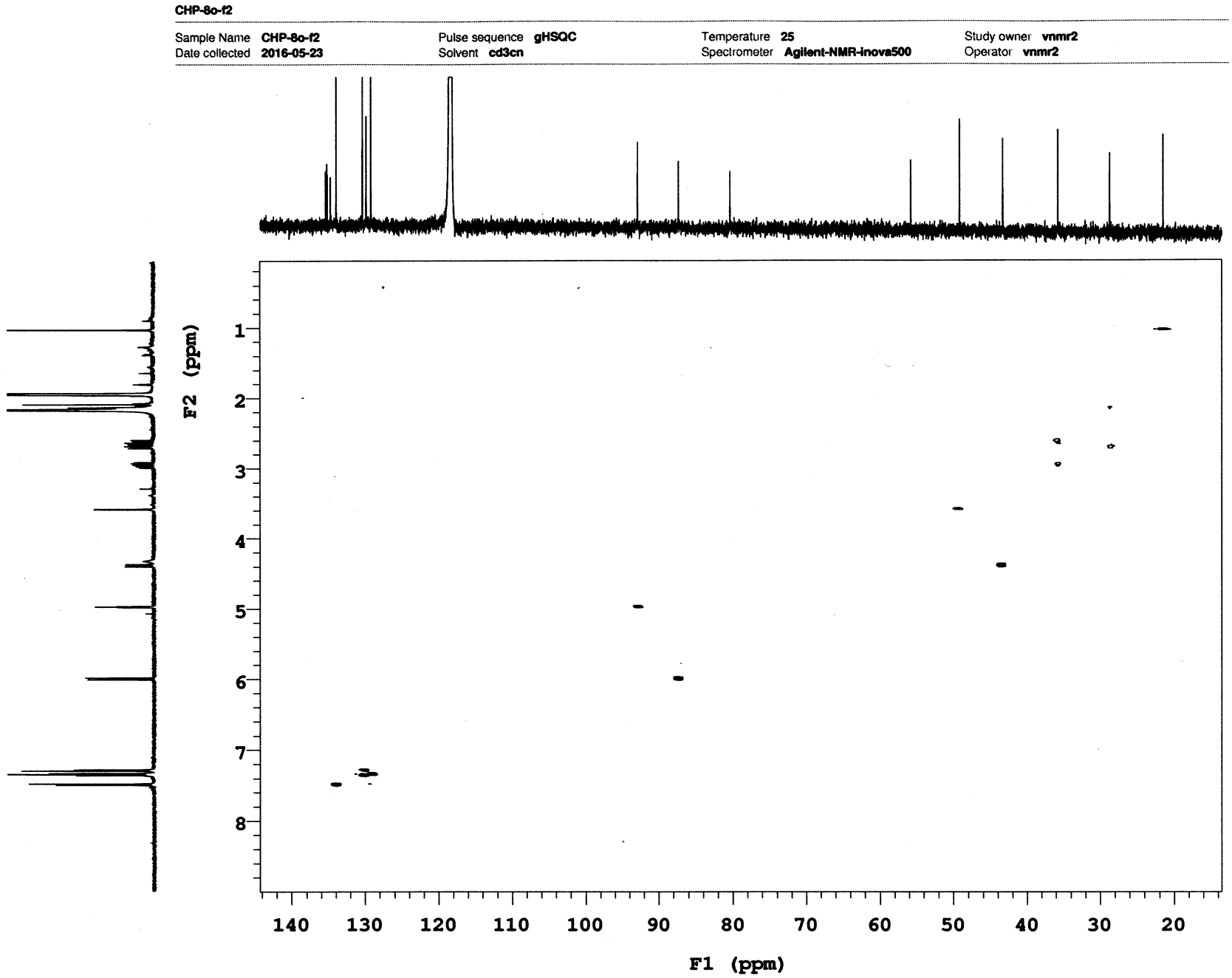
Fig S86. DEPT of compound 5e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8o-f2/DEPT_01.fid

Plot date 2016-05-27

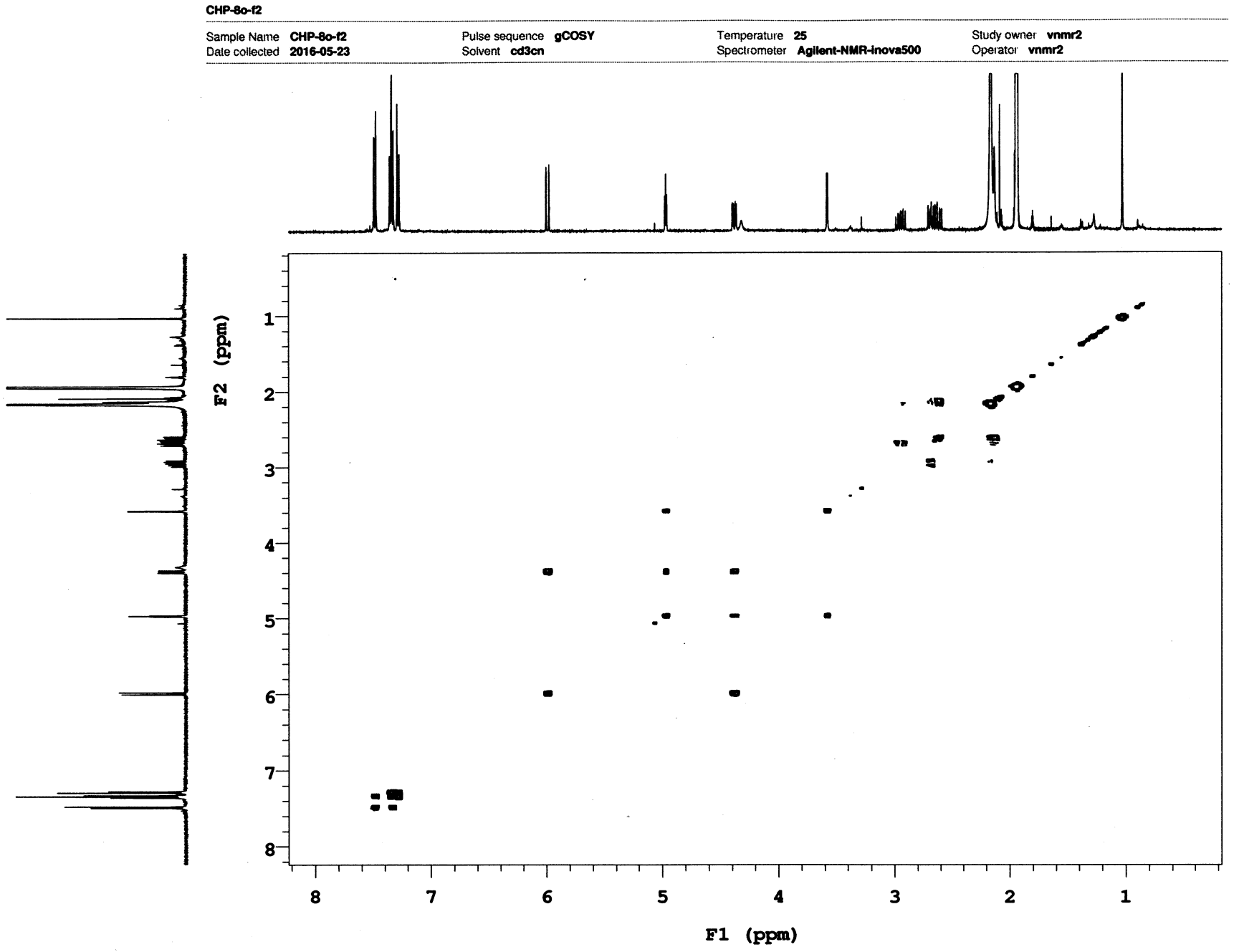
Fig S87. HSQC of compound 5e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8o-f2/gHSQC_01

Plot date 2016-05-27

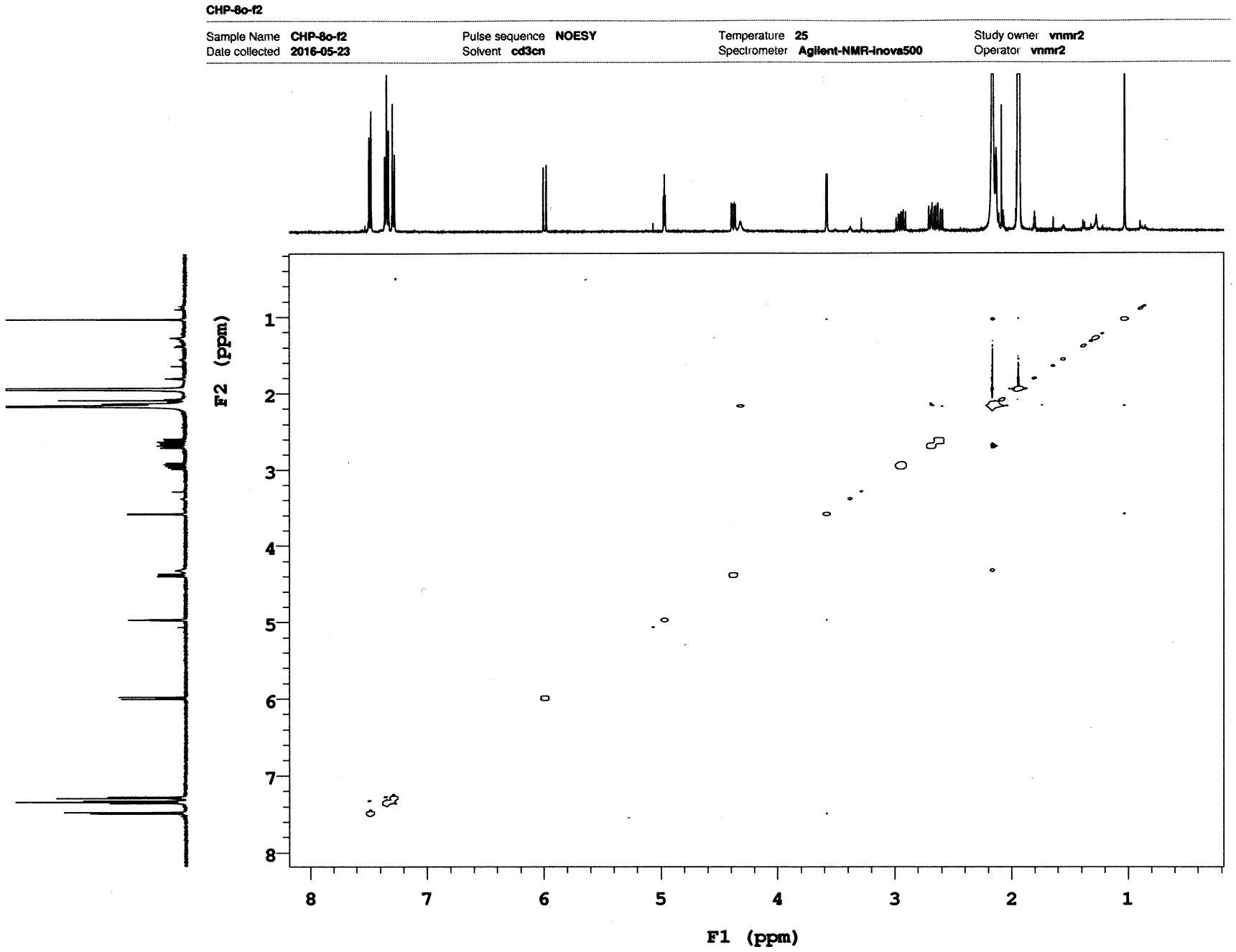
Fig S88. COSY of compound 5e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8o-f2/gCOSY_01

Plot date 2016-05-27

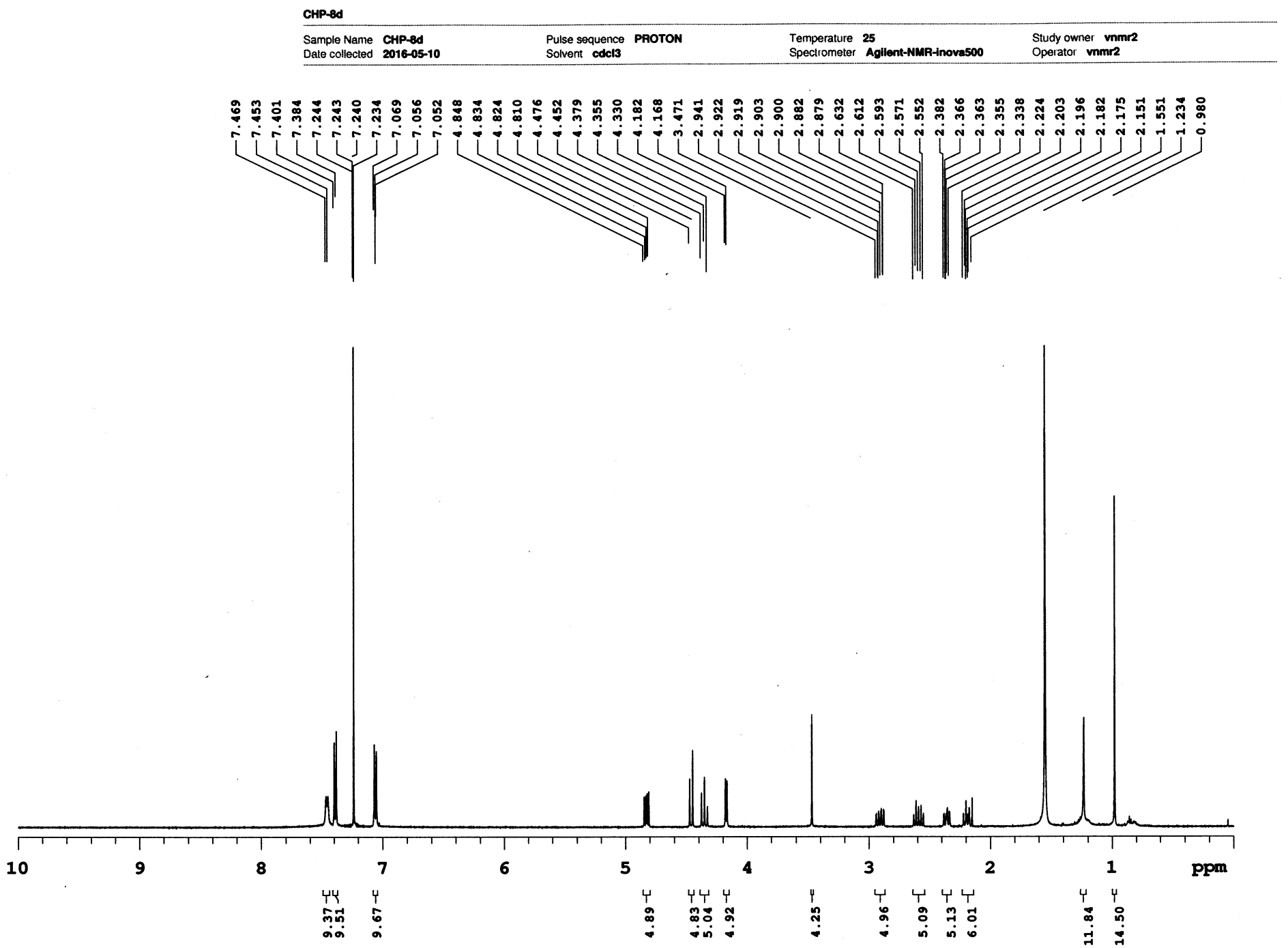
Fig S89. NOESY of compound 5e.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8o-f2/NOESY_01

Plot date 2016-05-27

Fig S90. 1H NMR (CDCl3, 500 MHz) of compound 3f.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d/PROTON_24

Plot date 2016-05-11

Fig S91. 13C NMR (CDCl3, 125 MHz) of compound 3f.

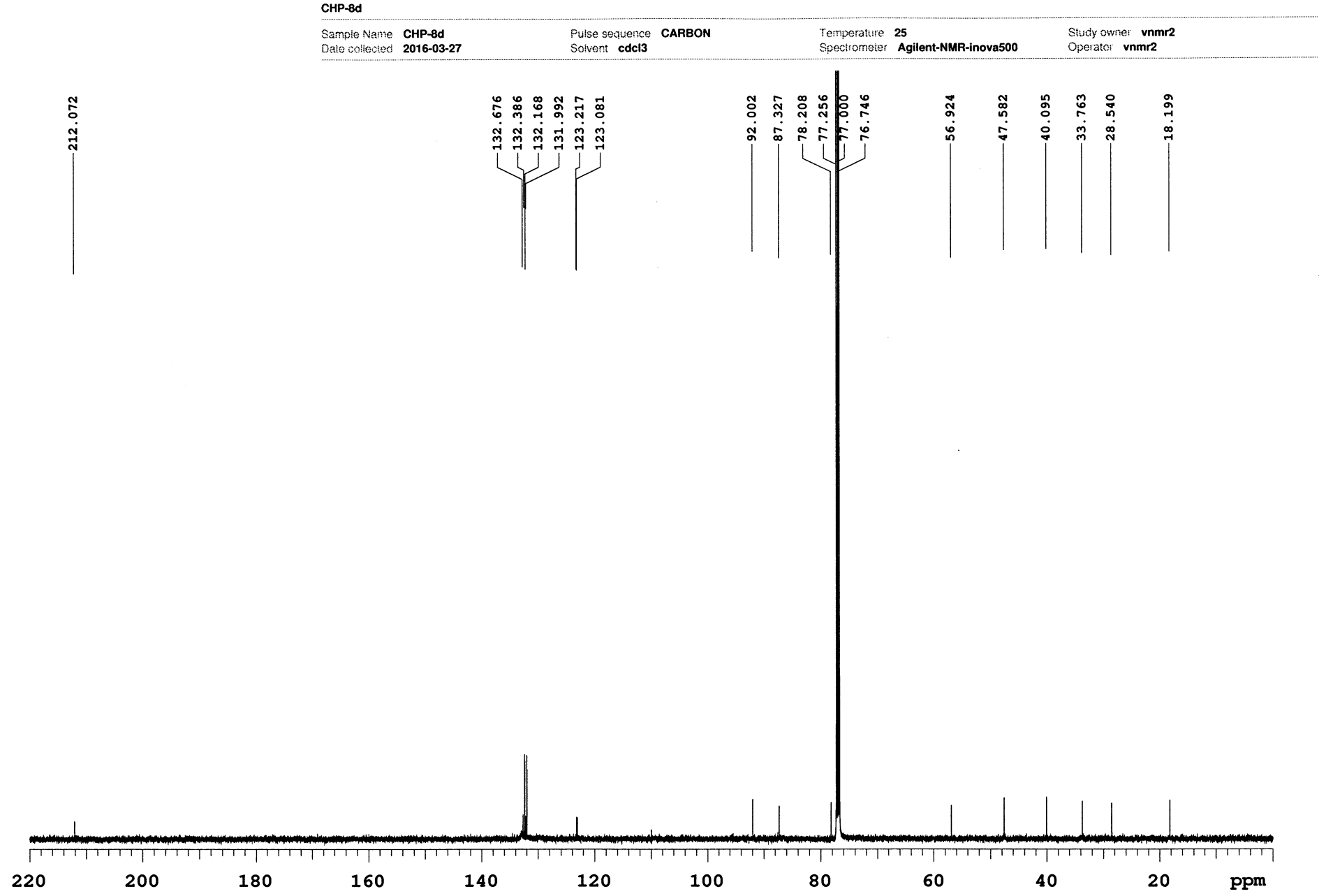
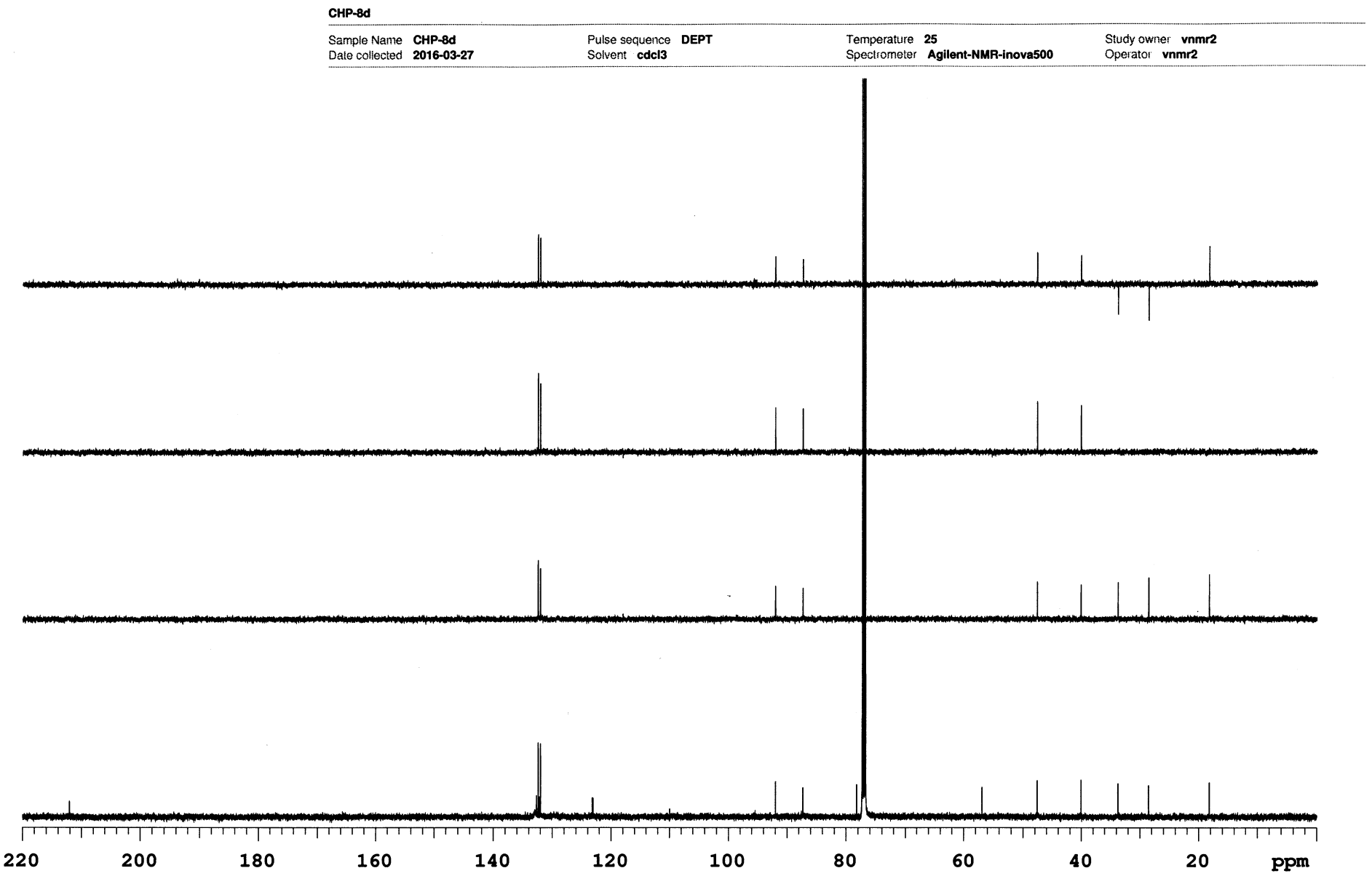


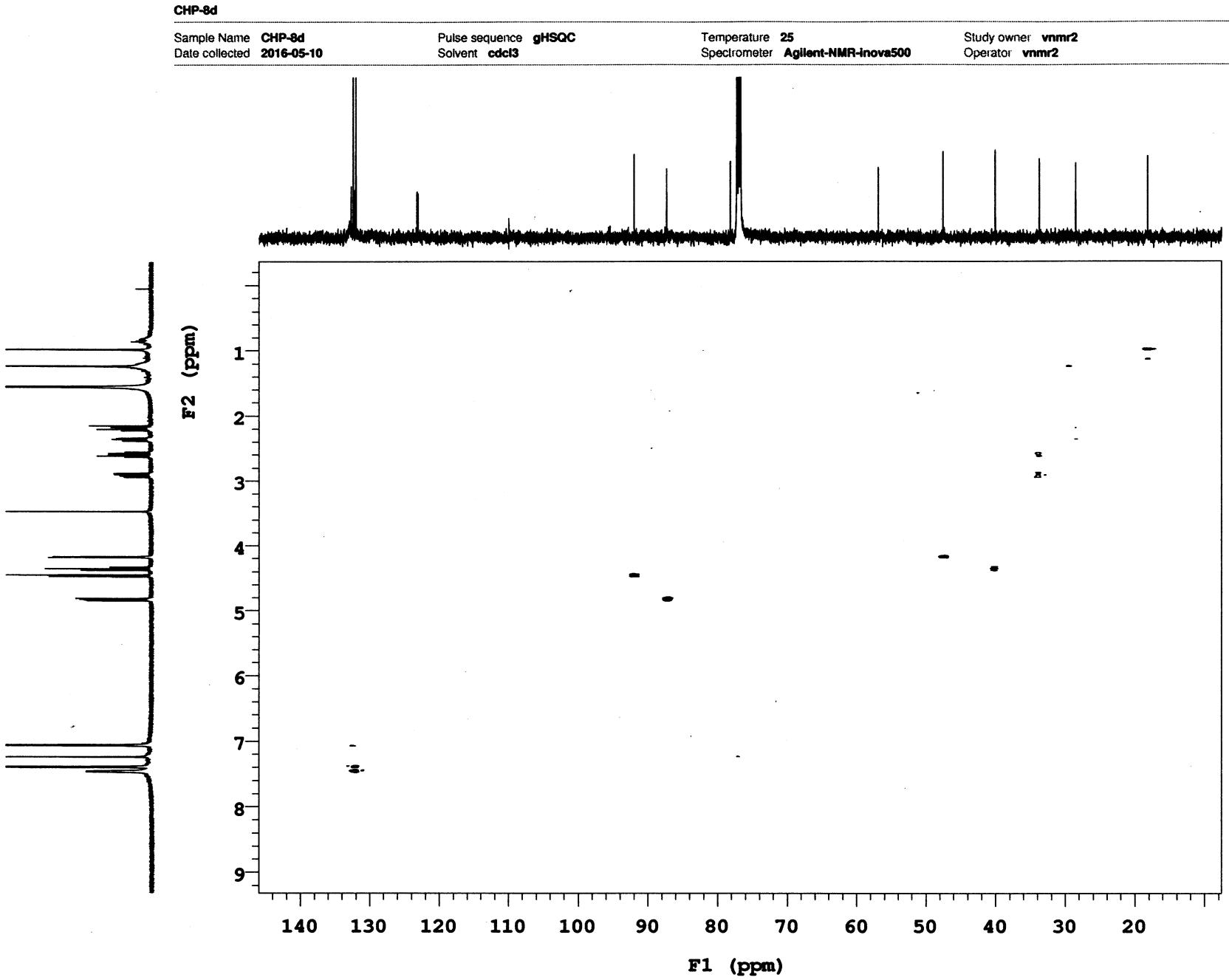
Fig S92. DEPT of compound 3f.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d/DEPT_01

Plot date 2016-03-29

Fig S93. HSQC of compound 3f.



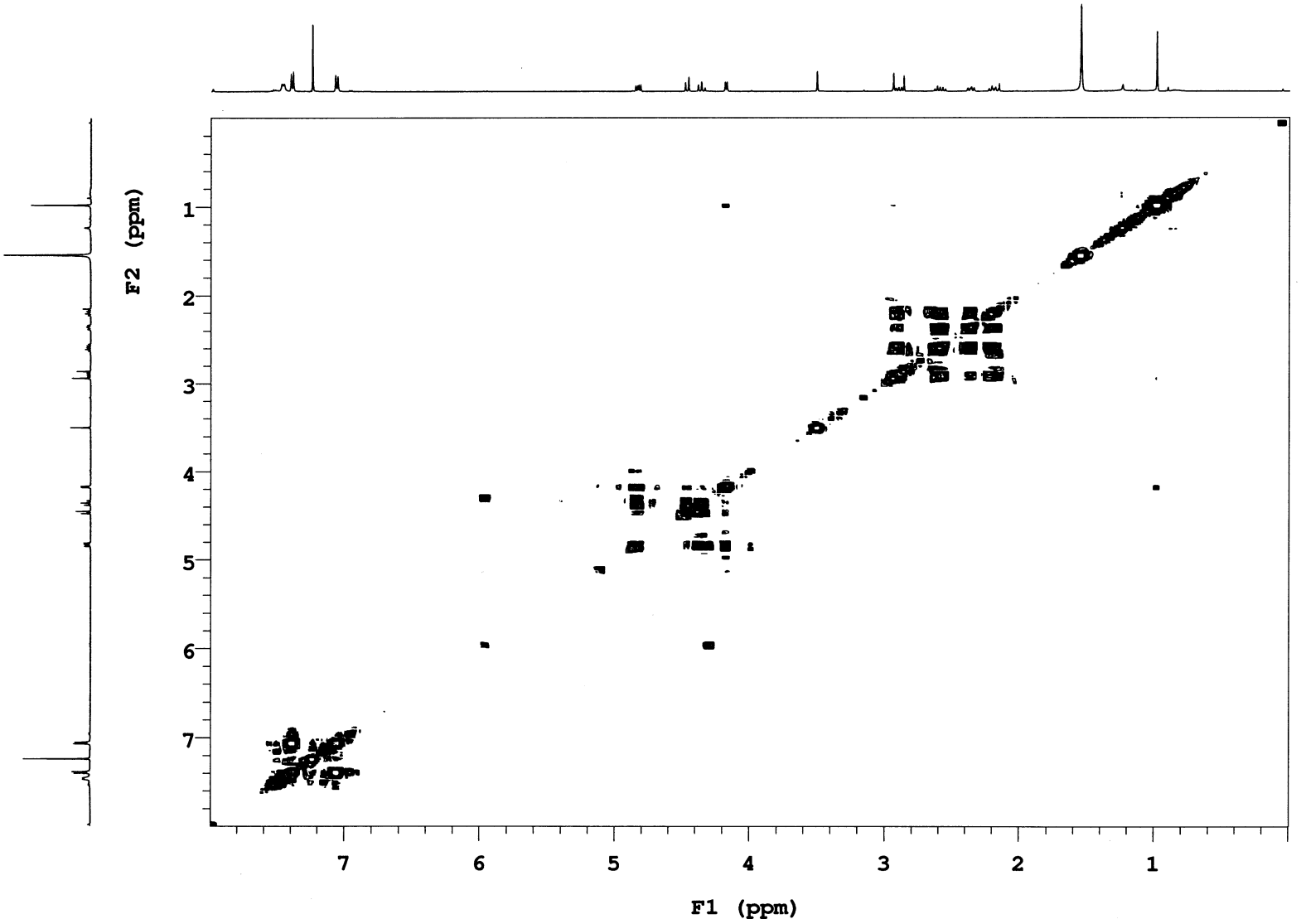
Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d/gHSQC_04

Plot date 2016-05-11

Fig S94. COSY of compound 3f.

CHP-8d

Sample Name	**CHP-8d**	Pulse sequence	**gCOSY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-03-27**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



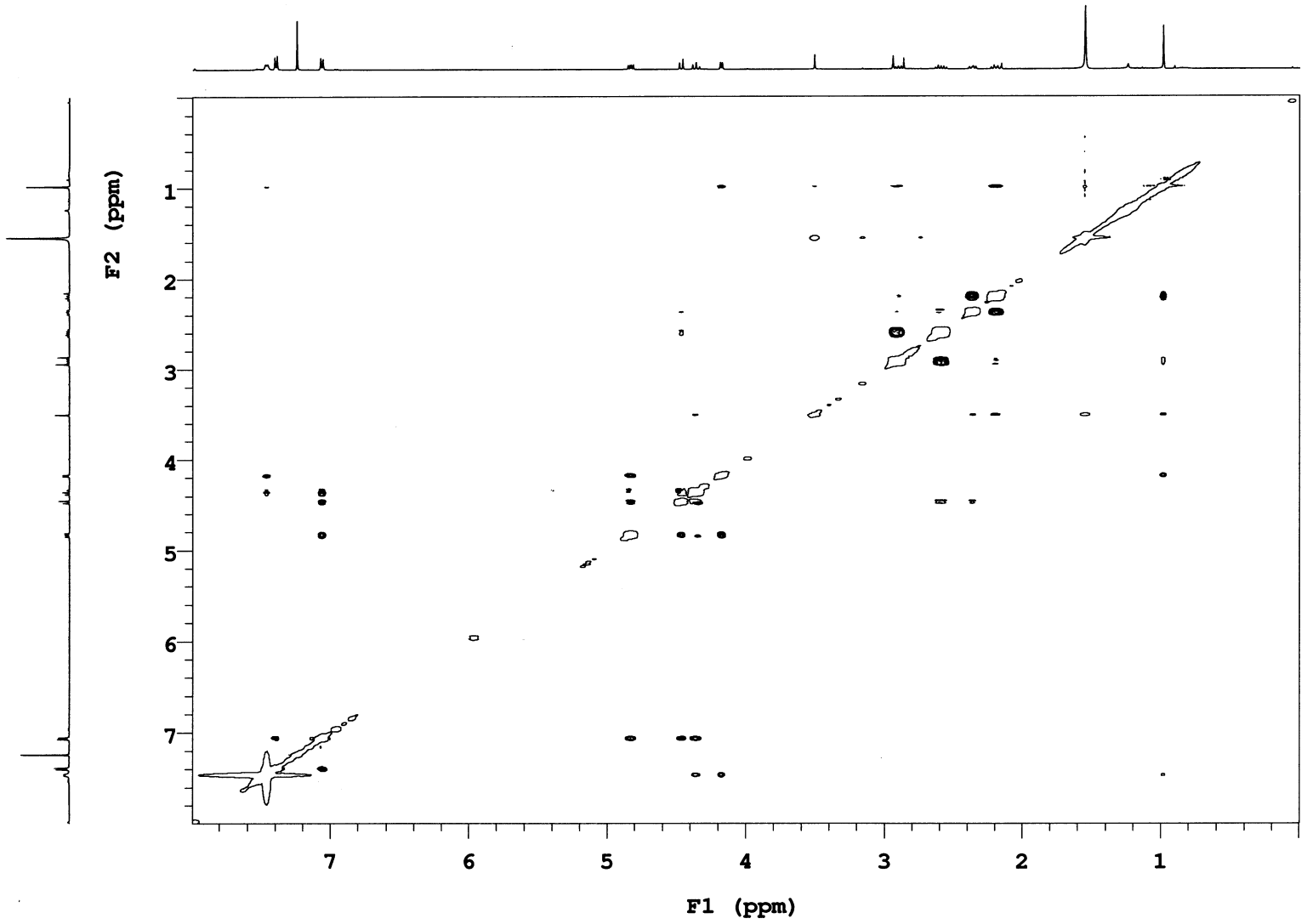
Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d/gCOSY_01

Plot date 2016-03-29

Fig S95. NOESY of compound 3f.

CHP-8d

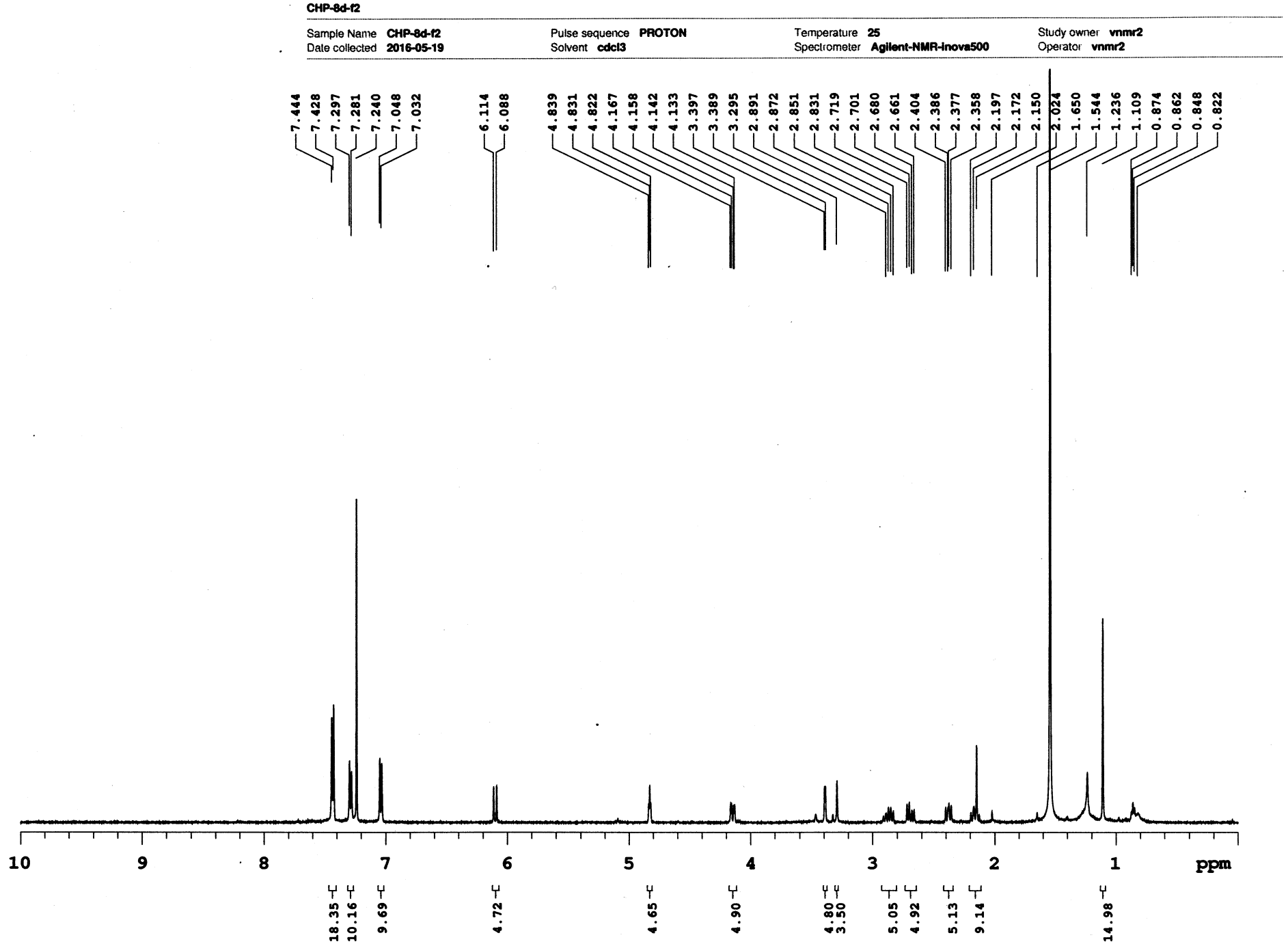
Sample Name	**CHP-8d**	Pulse sequence	**NOESY**	Temperature	**25**	Study owner	**vnmr2**
Date collected	**2016-03-27**	Solvent	**cdcl3**	Spectrometer	**Agilent-NMR-inova500**	Operator	**vnmr2**



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d/NOESY_01

Plot date 2016-03-29

Fig S96. 1H NMR (CDCl3, 500 MHz) of compound 5f.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d-f2/PROTON_09

Plot date 2016-05-20

Fig S97 13C NMR (CDCl3, 125 MHz) of compound 5f.

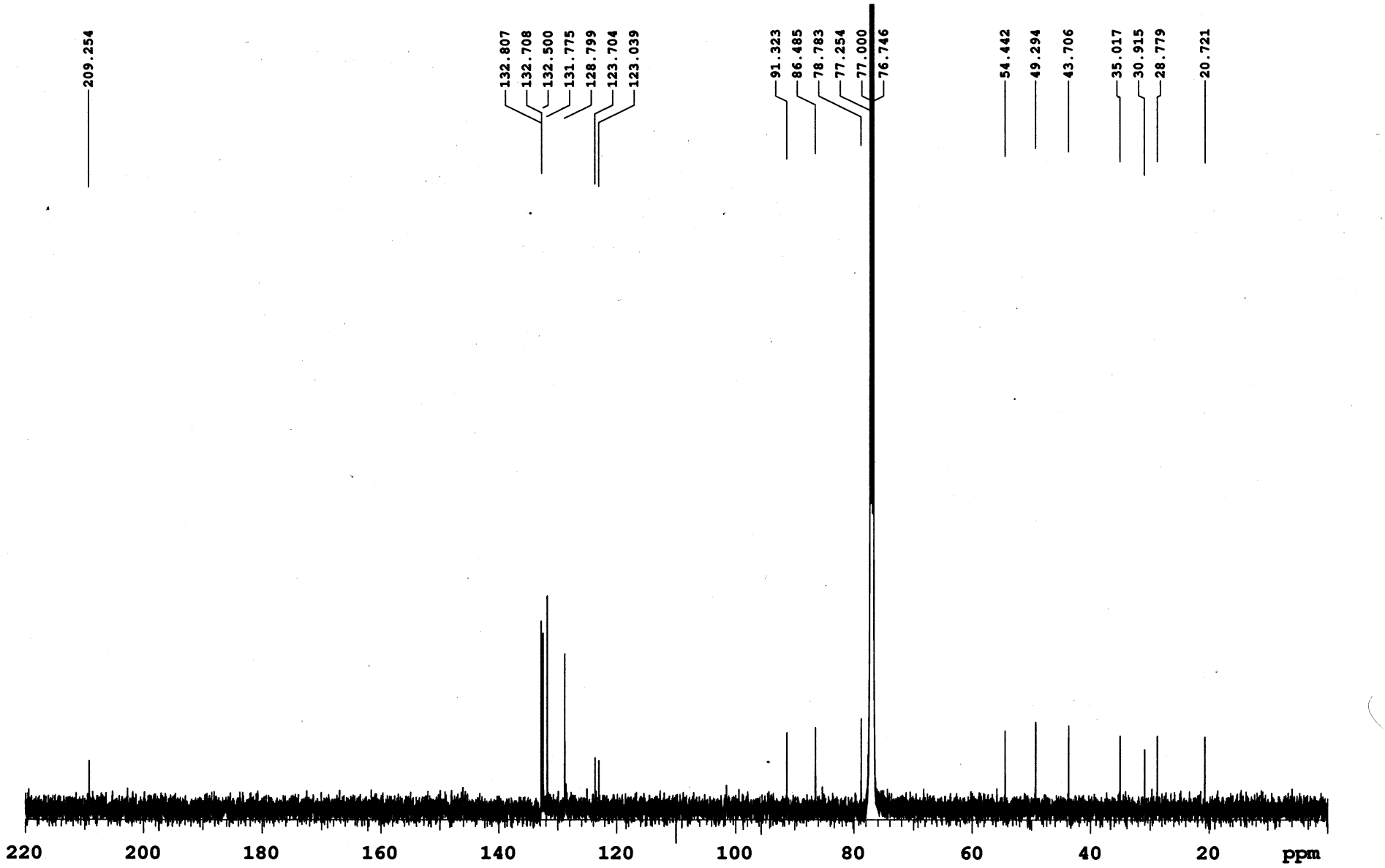
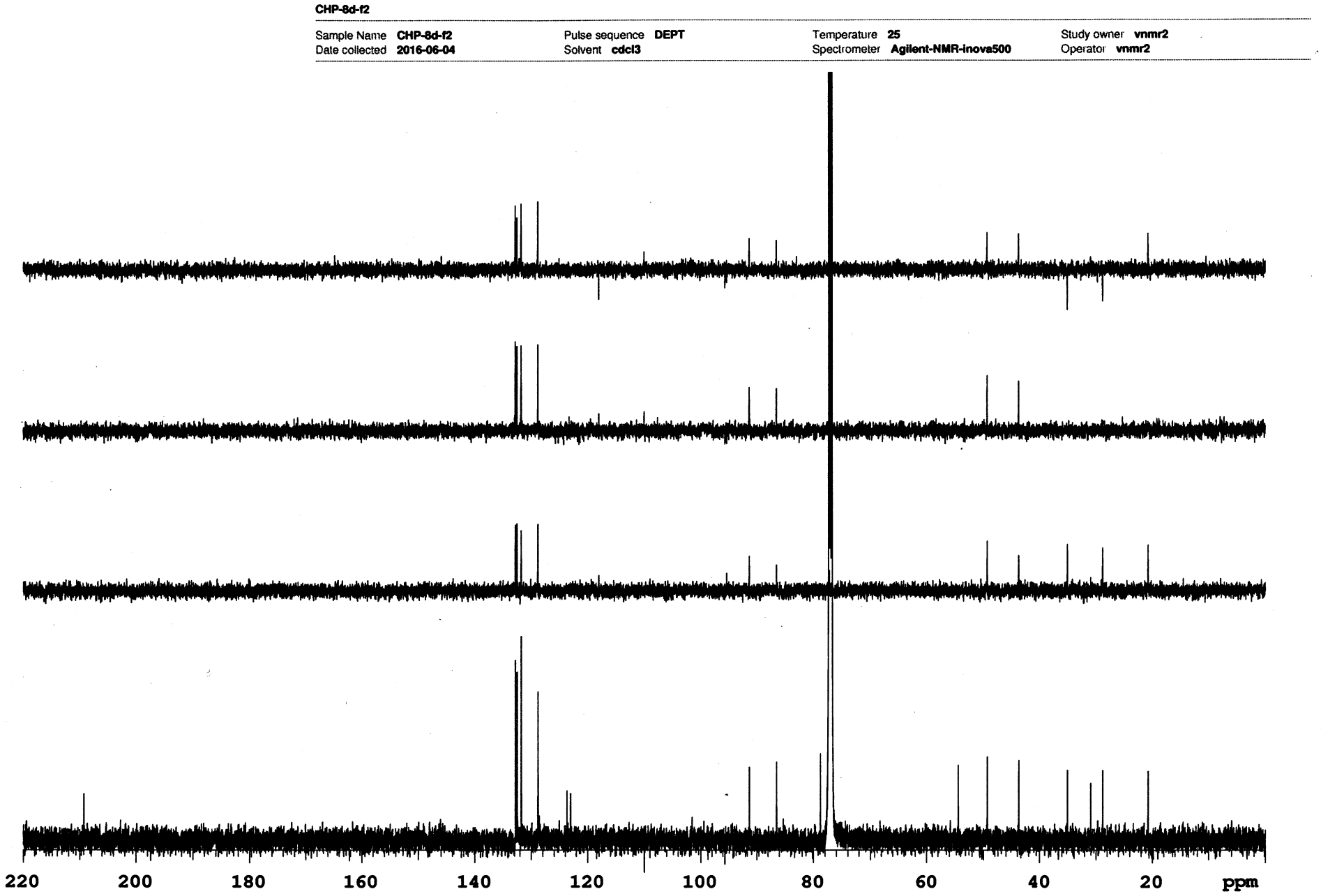


Fig S98. DEPT of compound 5f.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d-f2/DEPT_02

Plot date 2016-06-04

Fig S99. HSQC of compound 5f.

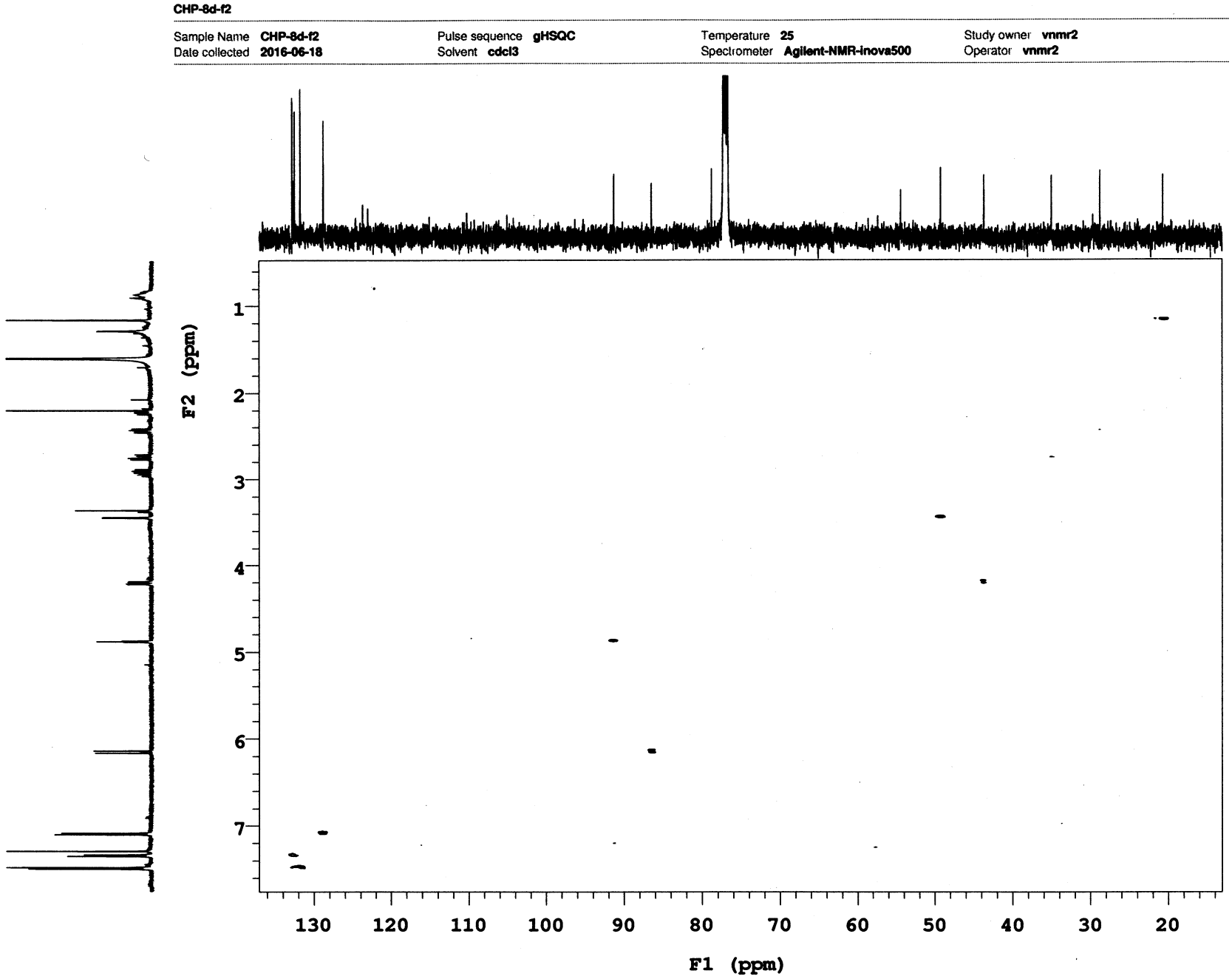
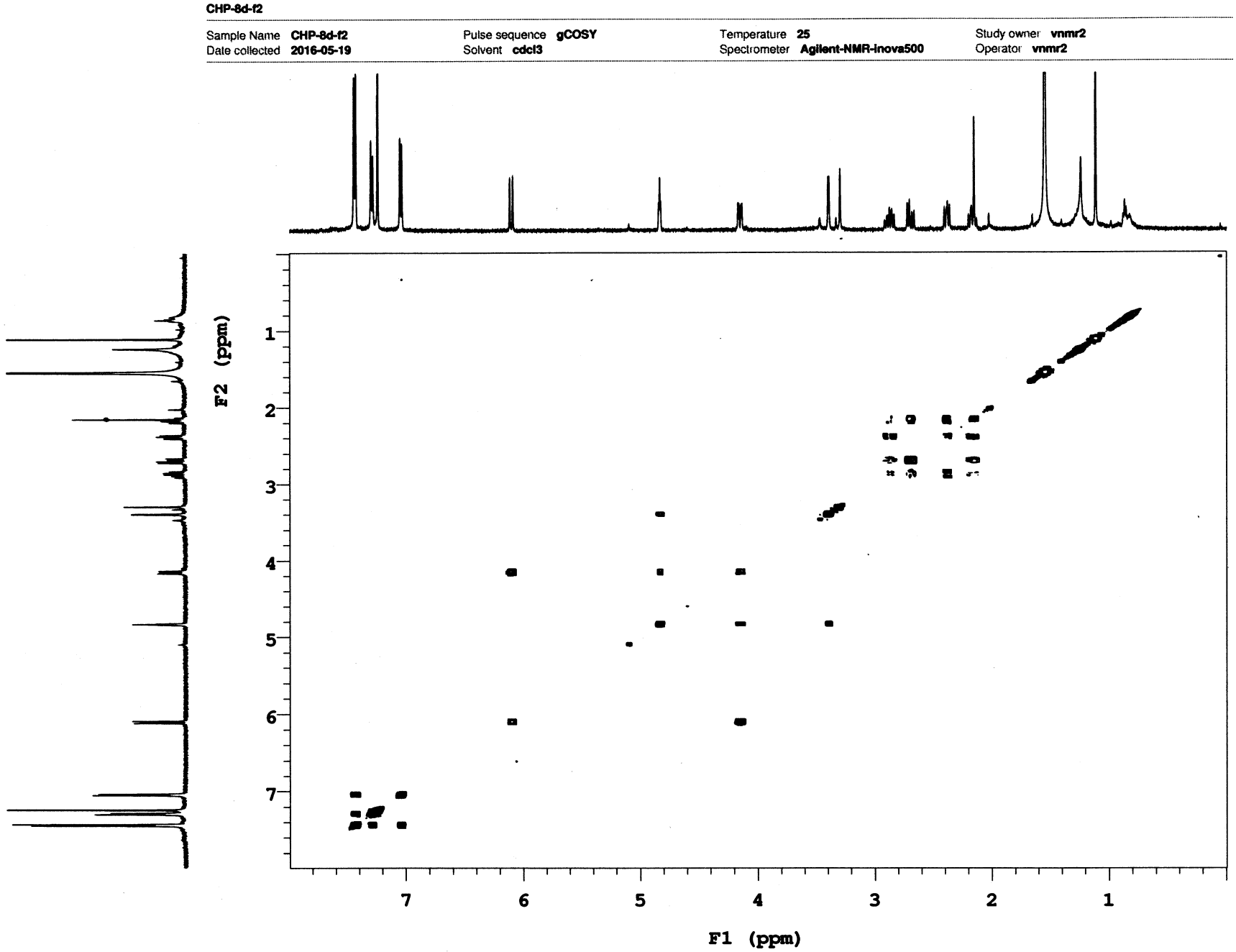


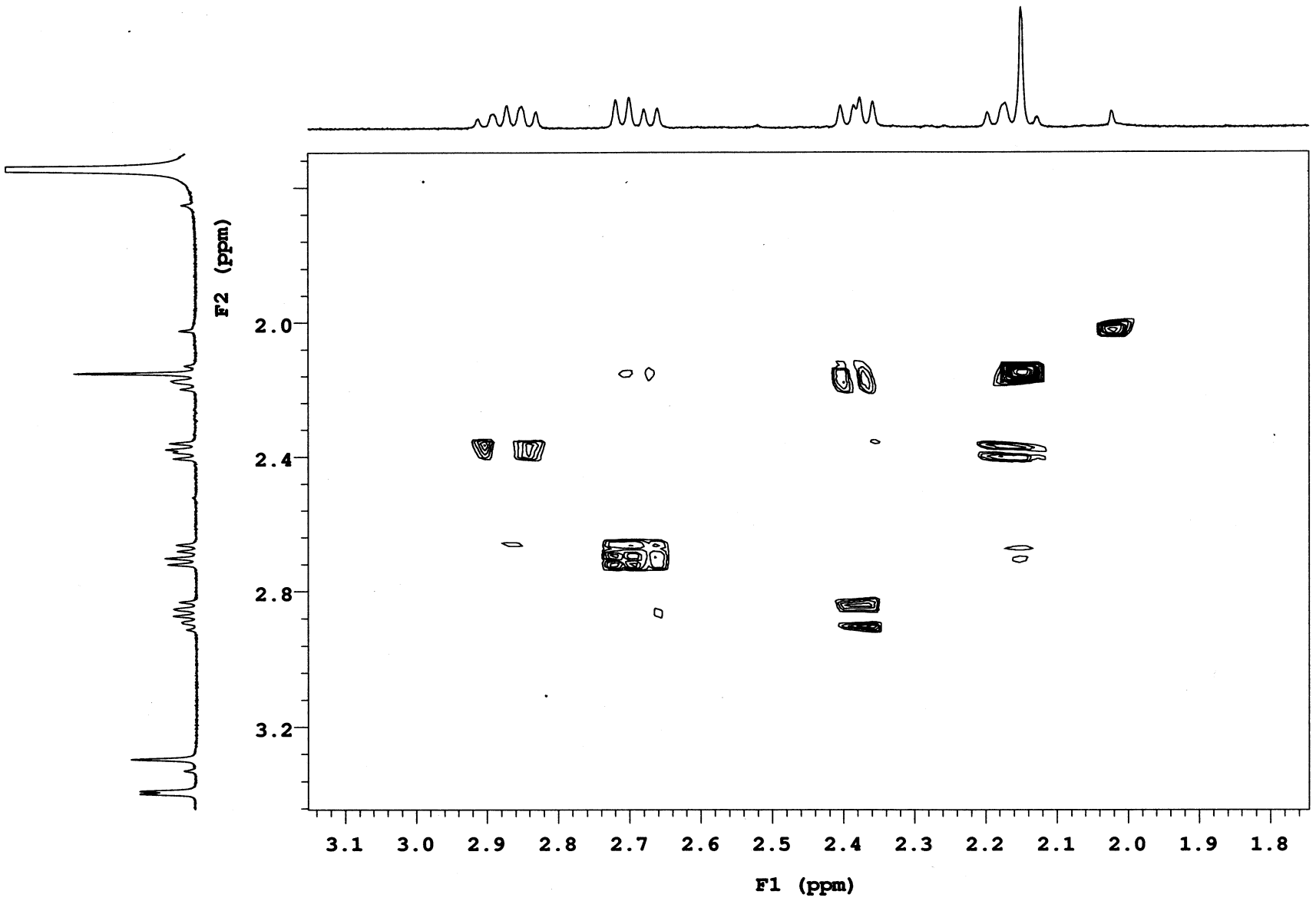
Fig S100. COSY of compound 5f.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d-f2/gCOSY_01

Plot date 2016-05-20

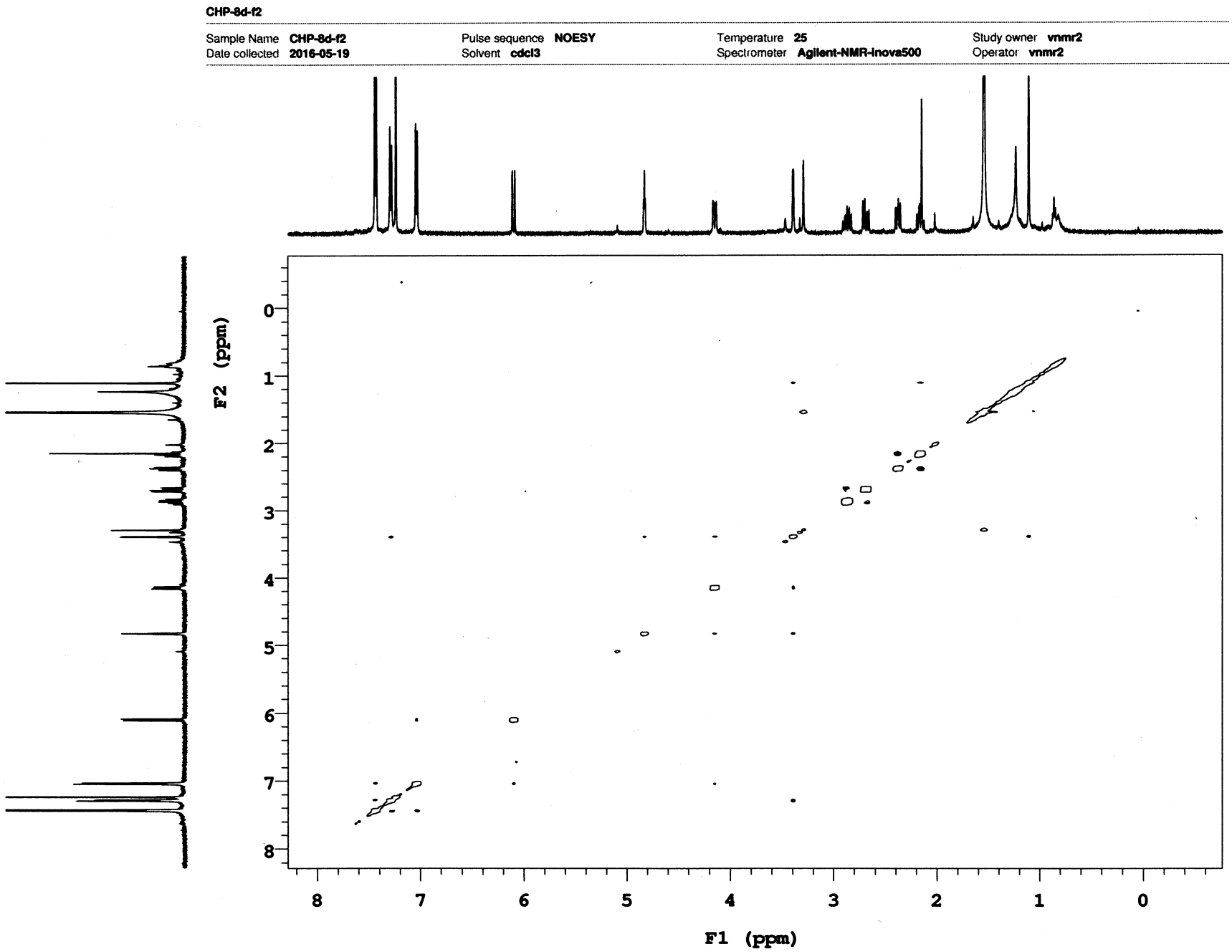
Fig S101. COSY of compound 5f, expanded.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d-f2/gCOSY_01

Plot date 2016-05-20

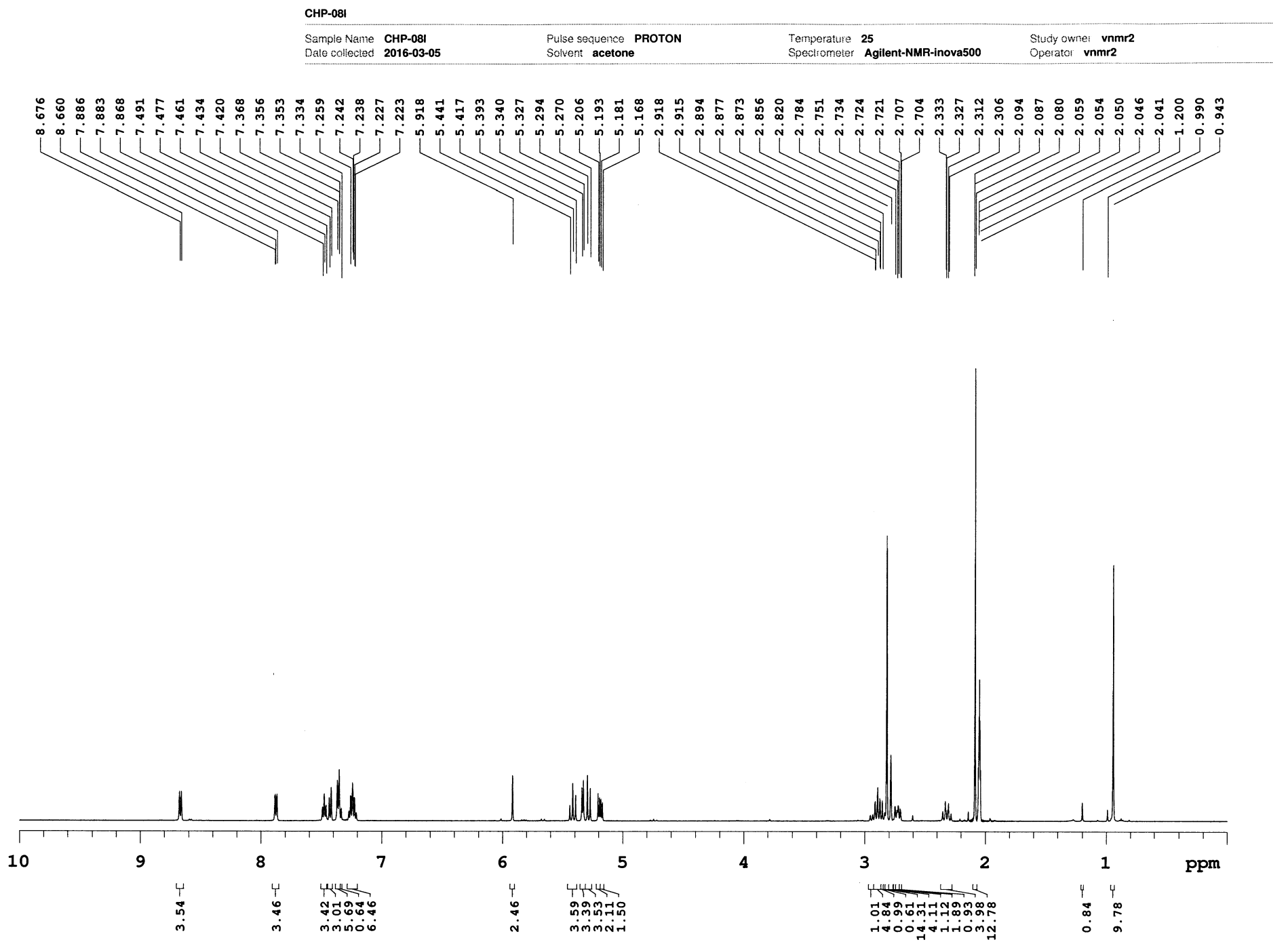
Fig S102. NOESY of compound 5f.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8d-f2/NOESY_01

Plot date 2016-05-20

Fig S103. 1H NMR (acetone-d6, 500 MHz) of compound 3g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-08I/PROTON_03

Plot date 2016-03-10

Fig S104. 13C NMR (acetone-d6, 125 MHz) of compound 3g.

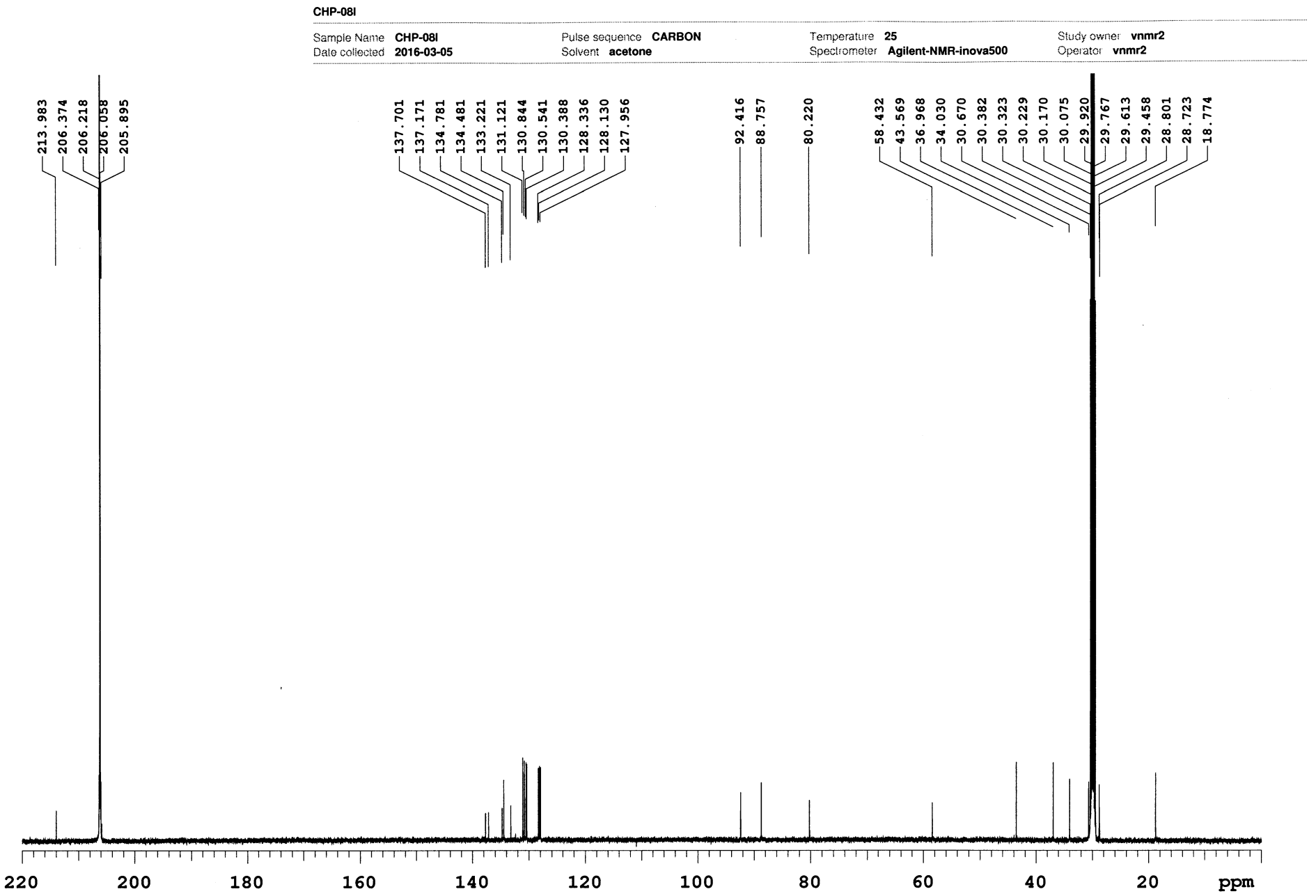
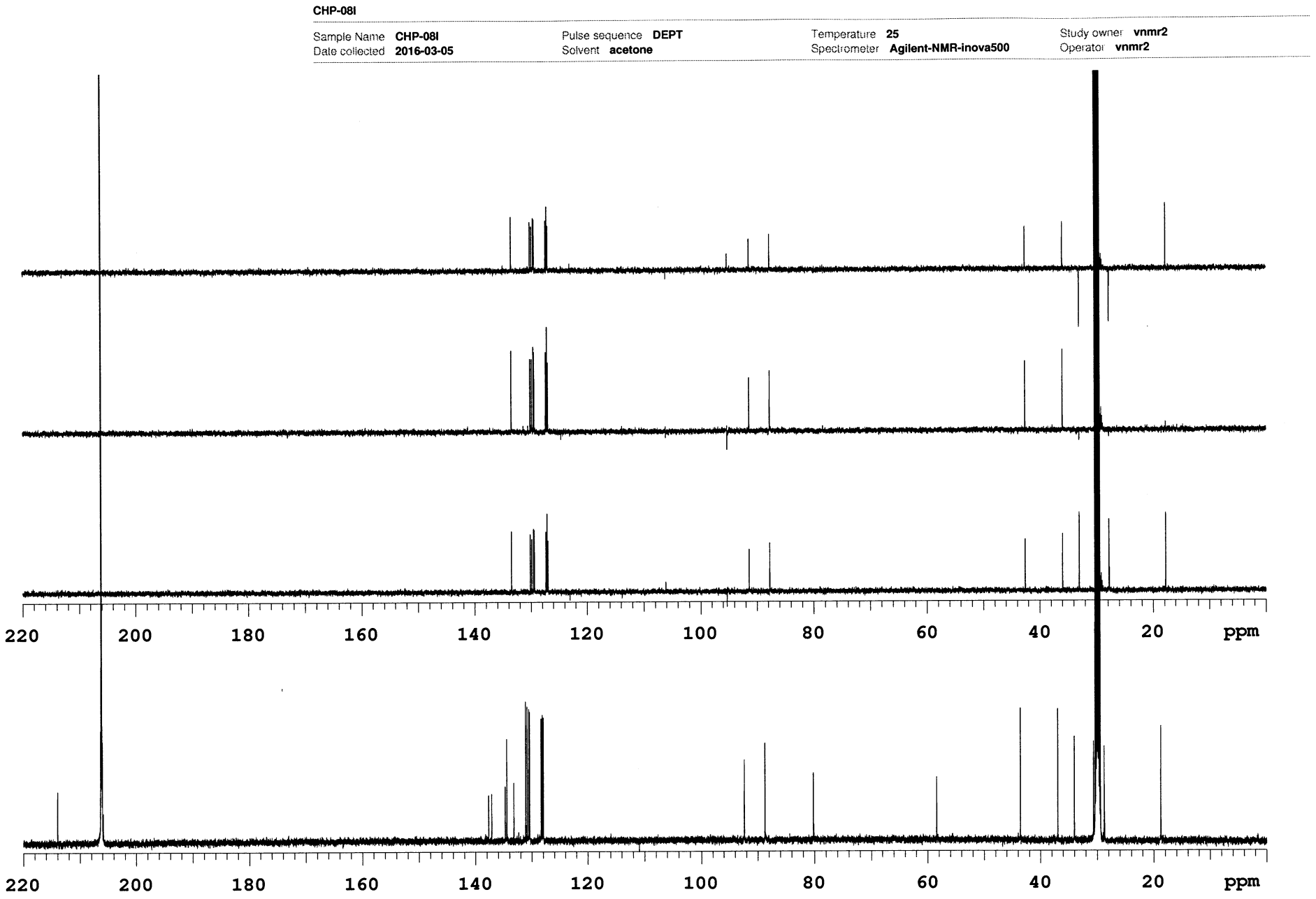


Fig S105. DEPT of compound 3g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-08I/DEPT_01

Plot date 2016-03-13

Fig S106. HSQC of compound 3g.

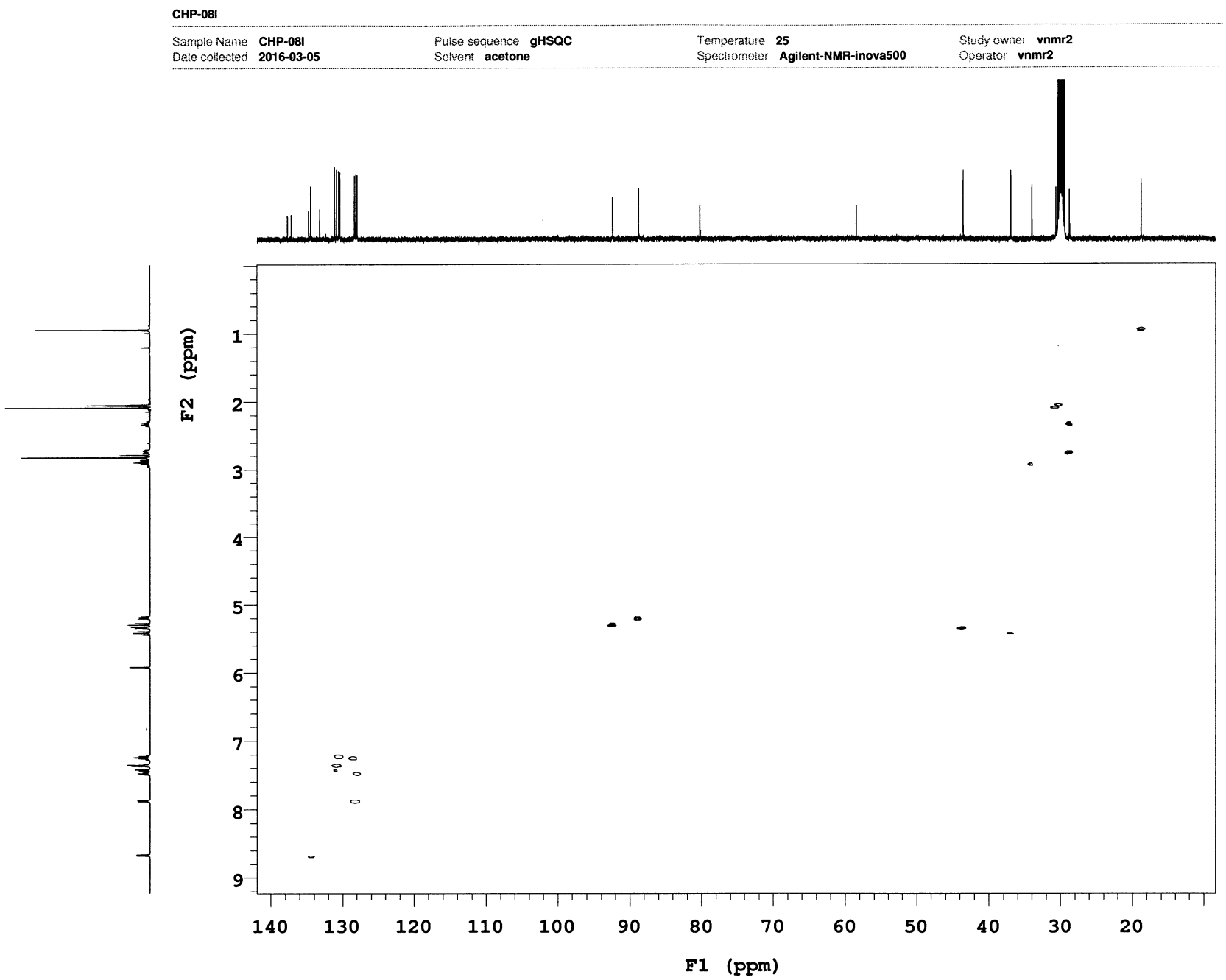
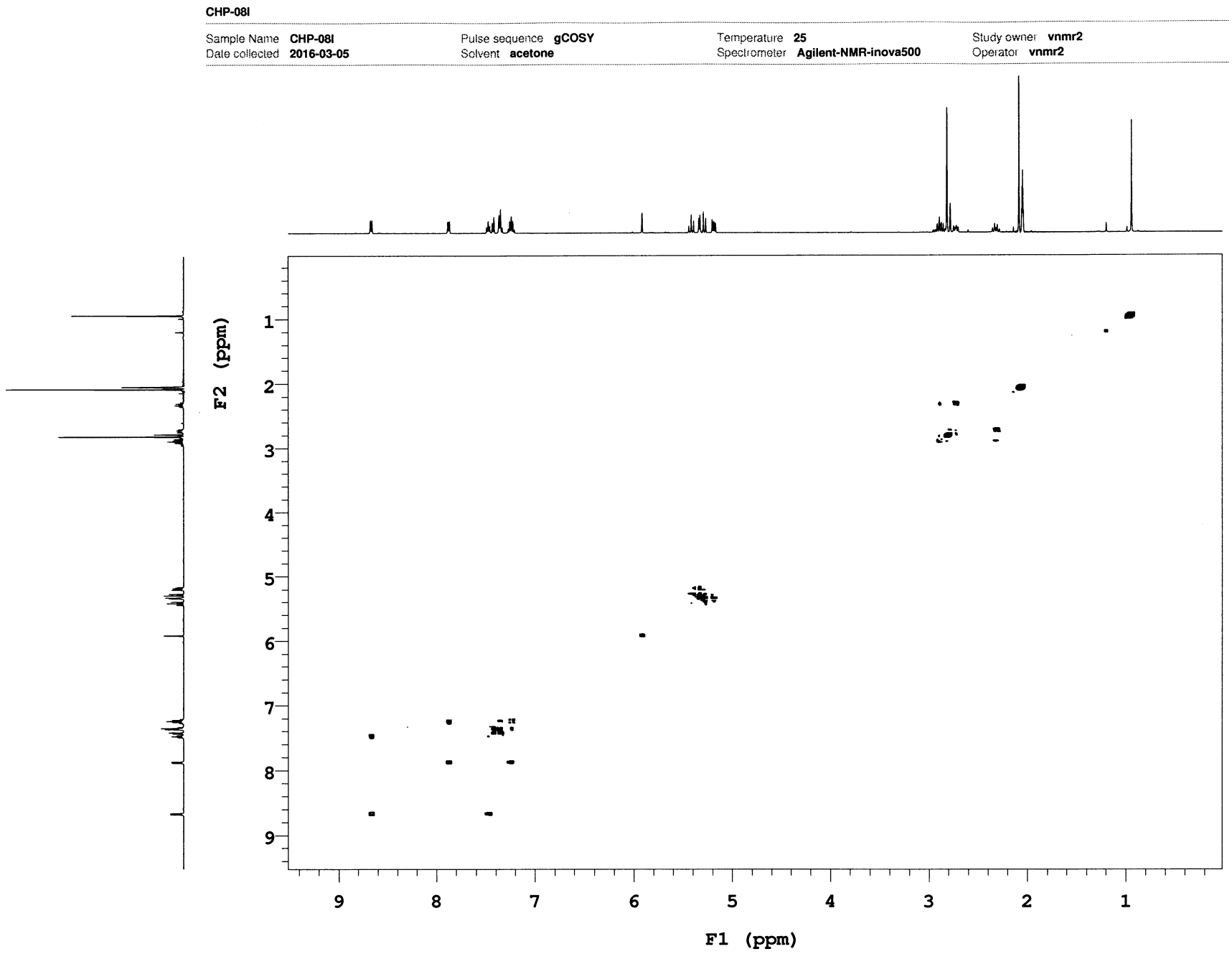


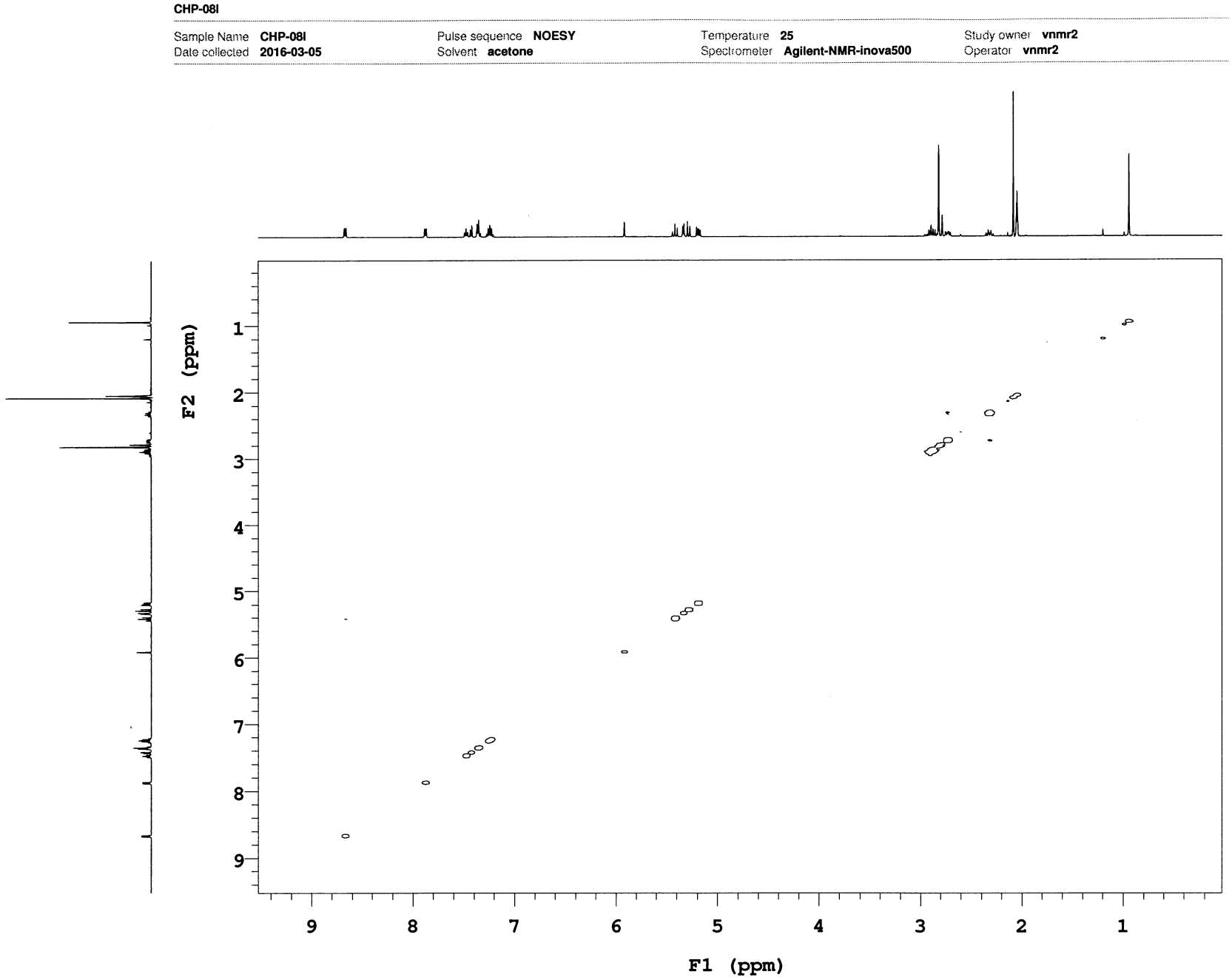
Fig S107. COSY of compound 3g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-08I/gCOSY_01

Plot date 2016-03-13

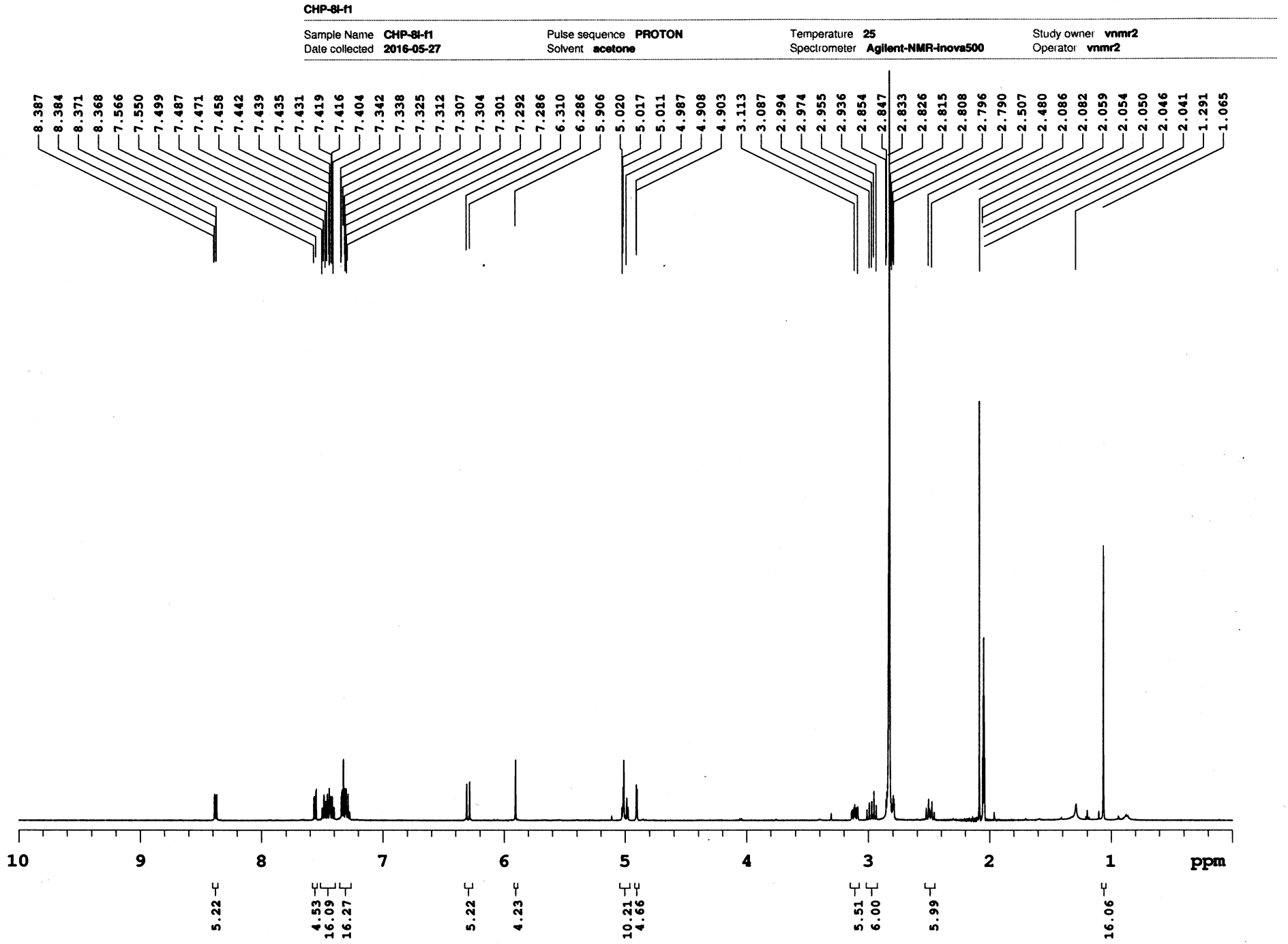
Fig S108. NOESY of compound 3g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-08I/NOESY_01

Plot date 2016-03-13

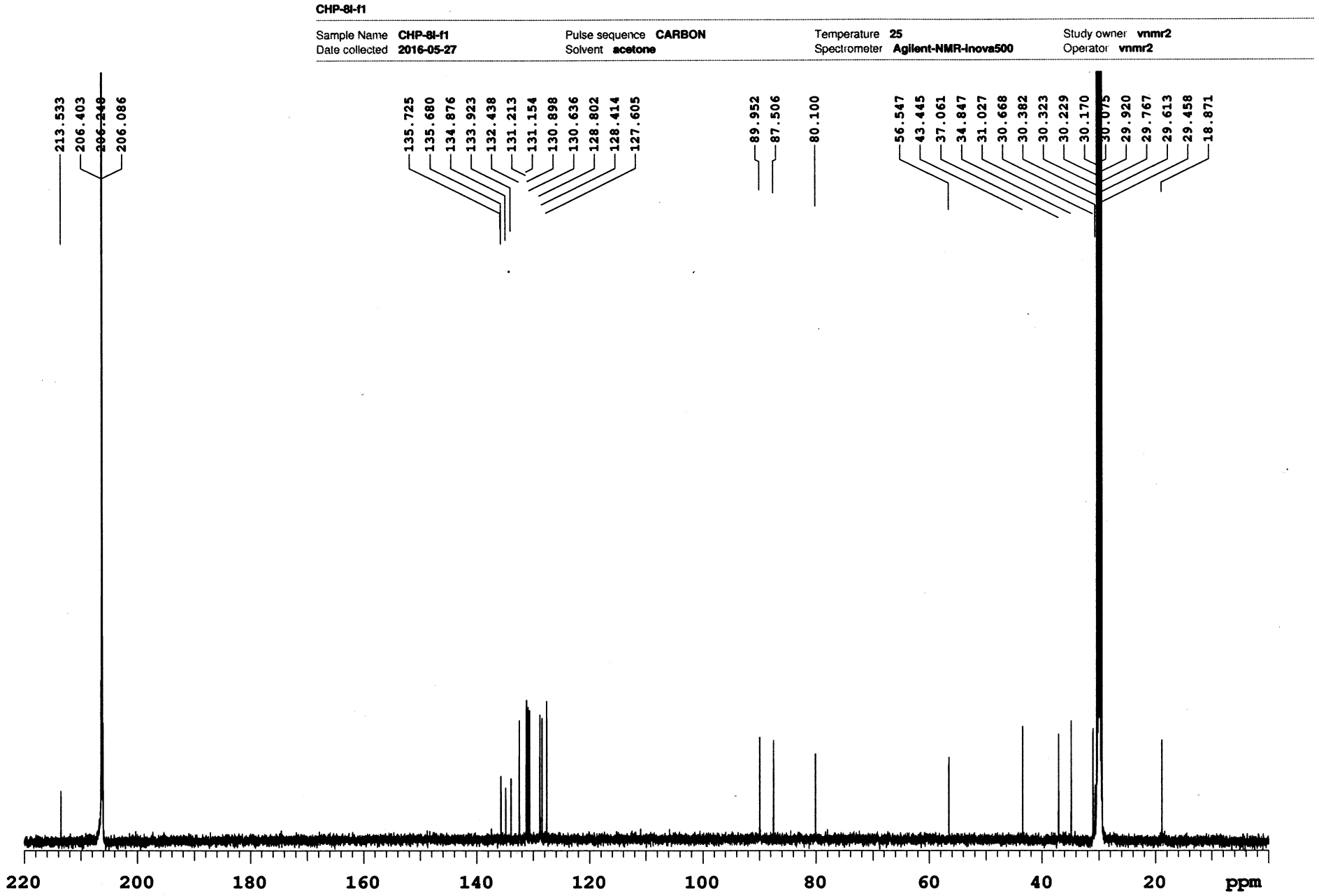
Fig S109. 1H NMR (acetone-d6, 500 MHz) of compound 5g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8I-f1/PROTON_05

Plot date 2016-05-27

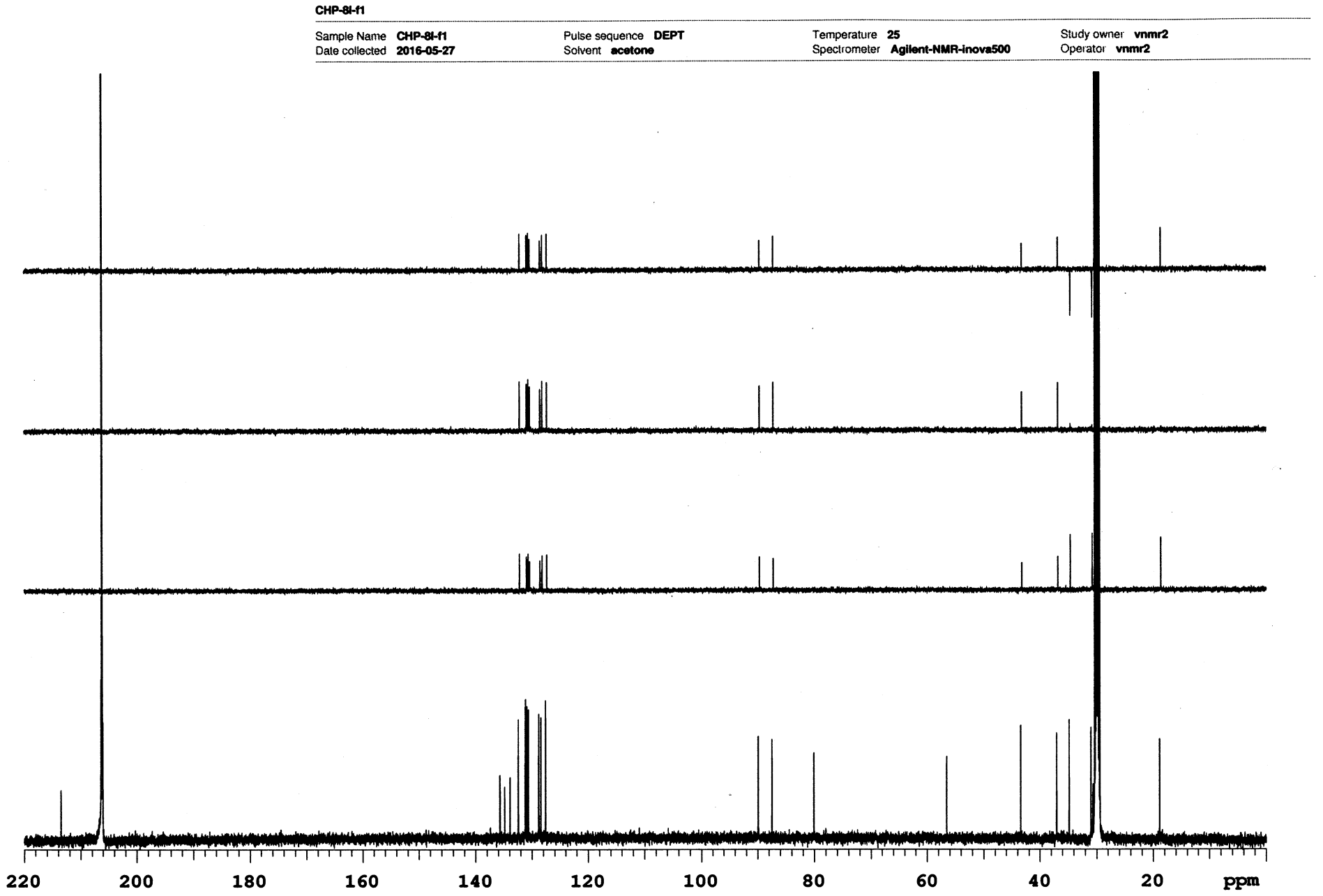
Fig S110. 13C NMR (acetone-d6, 125 MHz) of compound 5g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8I-f1/CARBON_01

Plot date 2016-05-27

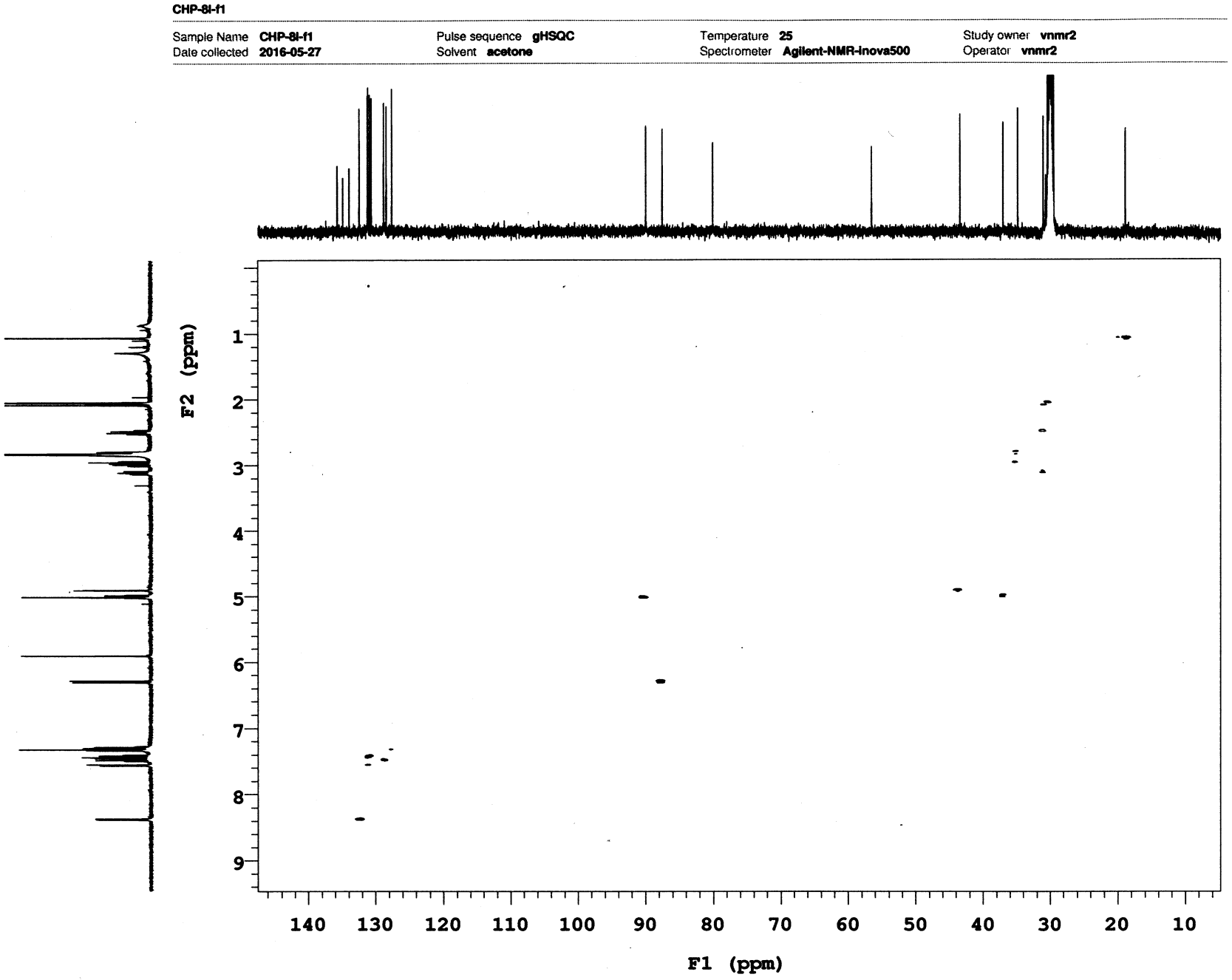
Fig S111. DEPT of compound 5g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8I-f1/DEPT_01

Plot date 2016-05-27

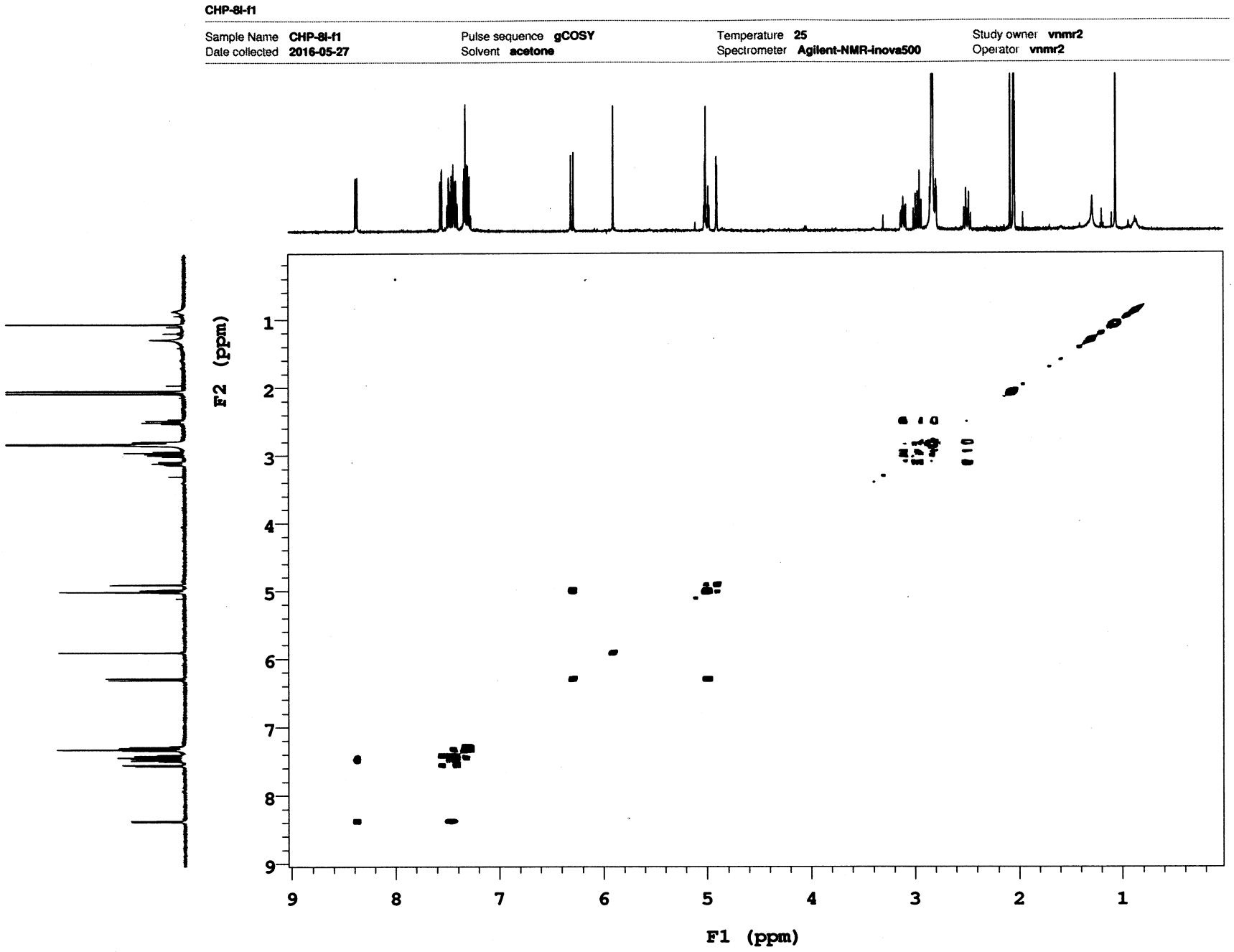
Fig S112. HSQC of compound 5g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8I-f1/gHSQC_01

Plot date 2016-05-27

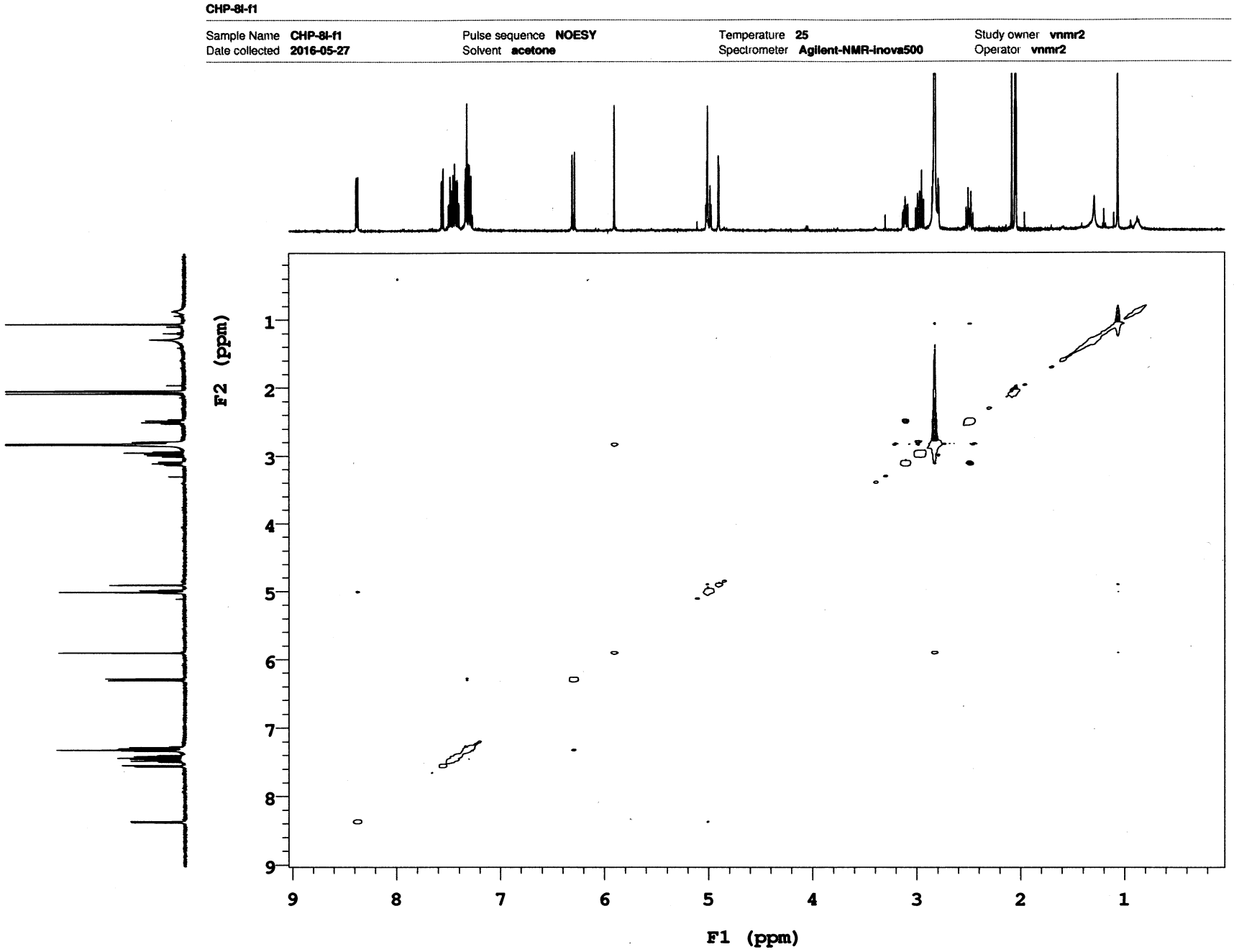
Fig S113. COSY of compound 5g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8I-f1/gCOSY_01

Plot date 2016-05-27

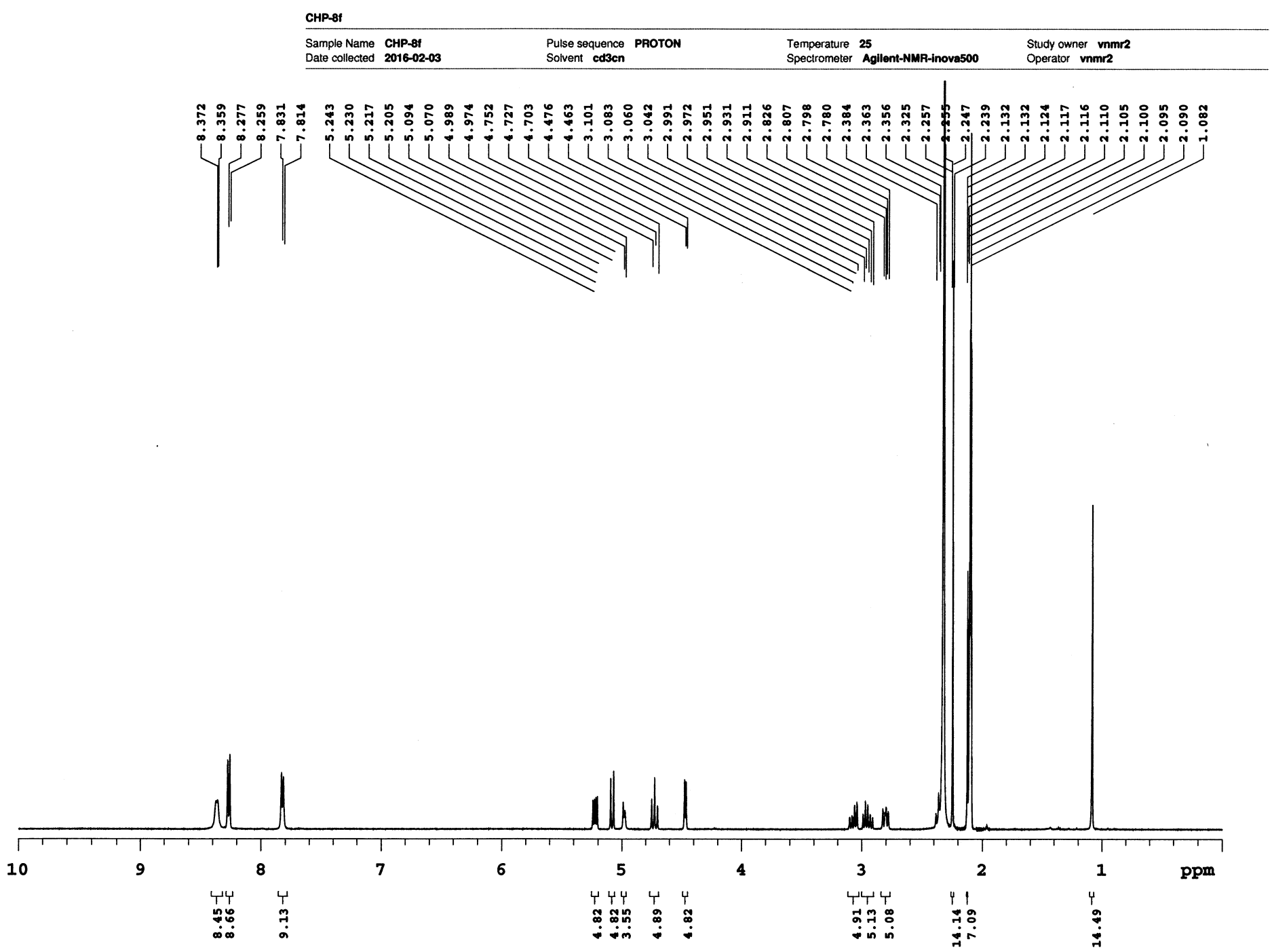
Fig S114. NOESY of compound 5g.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8l-f1/NOESY_01

Plot date 2016-05-27

Fig S115. 1H NMR (CD3CN, 500 MHz) of compound 3h.



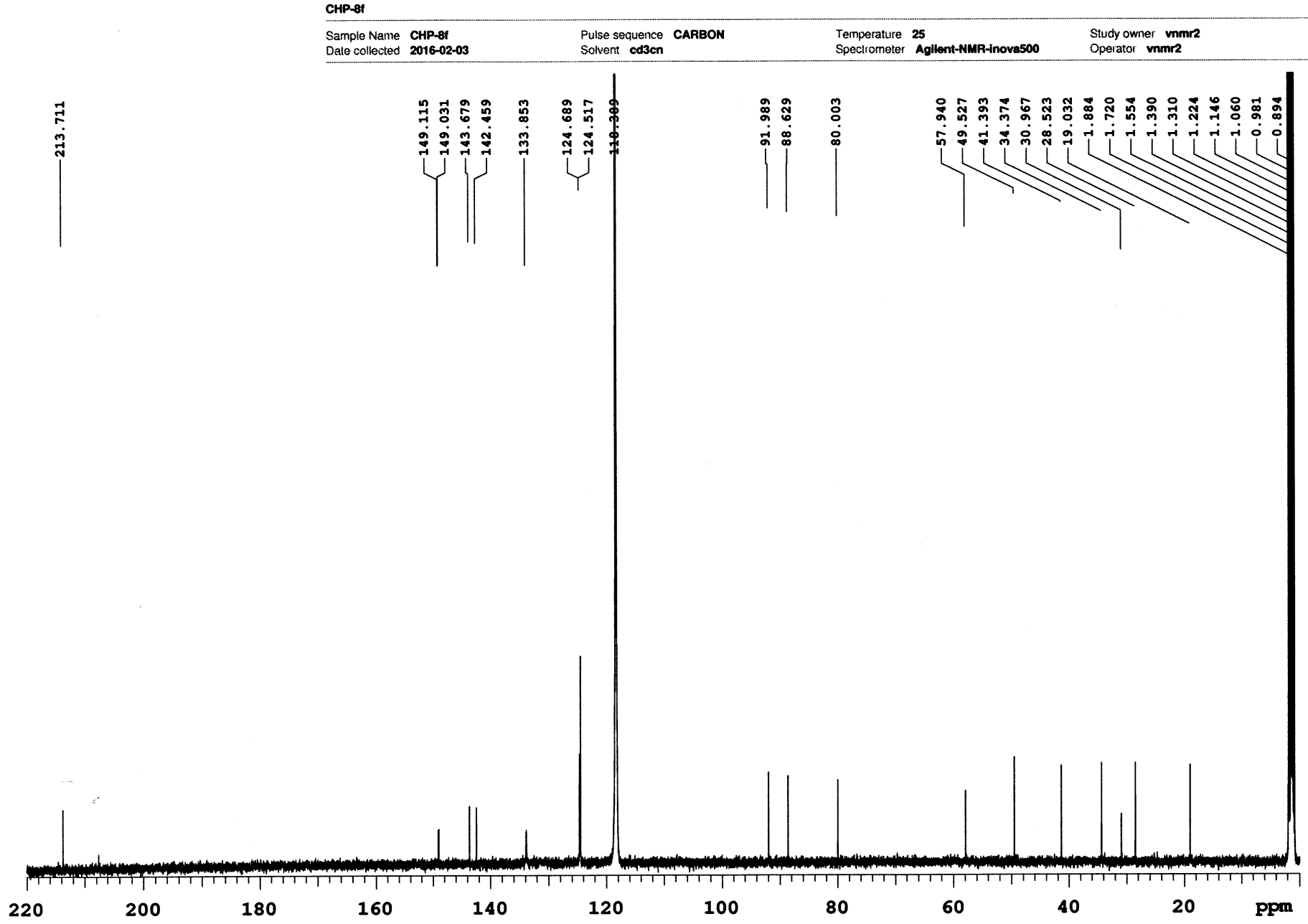


Fig S116. 13C NMR (CD3CN, 125 MHz) of compound 3h.

CHP-8f

Sample Name **CHP-8f** | Pulse sequence **DEPT** | Temperature **25** | Study owner **vnmr2**
Date collected **2016-02-04** | Solvent **cd3cn** | Spectrometer **Agilent-NMR-inova500** | Operator **vnmr2**

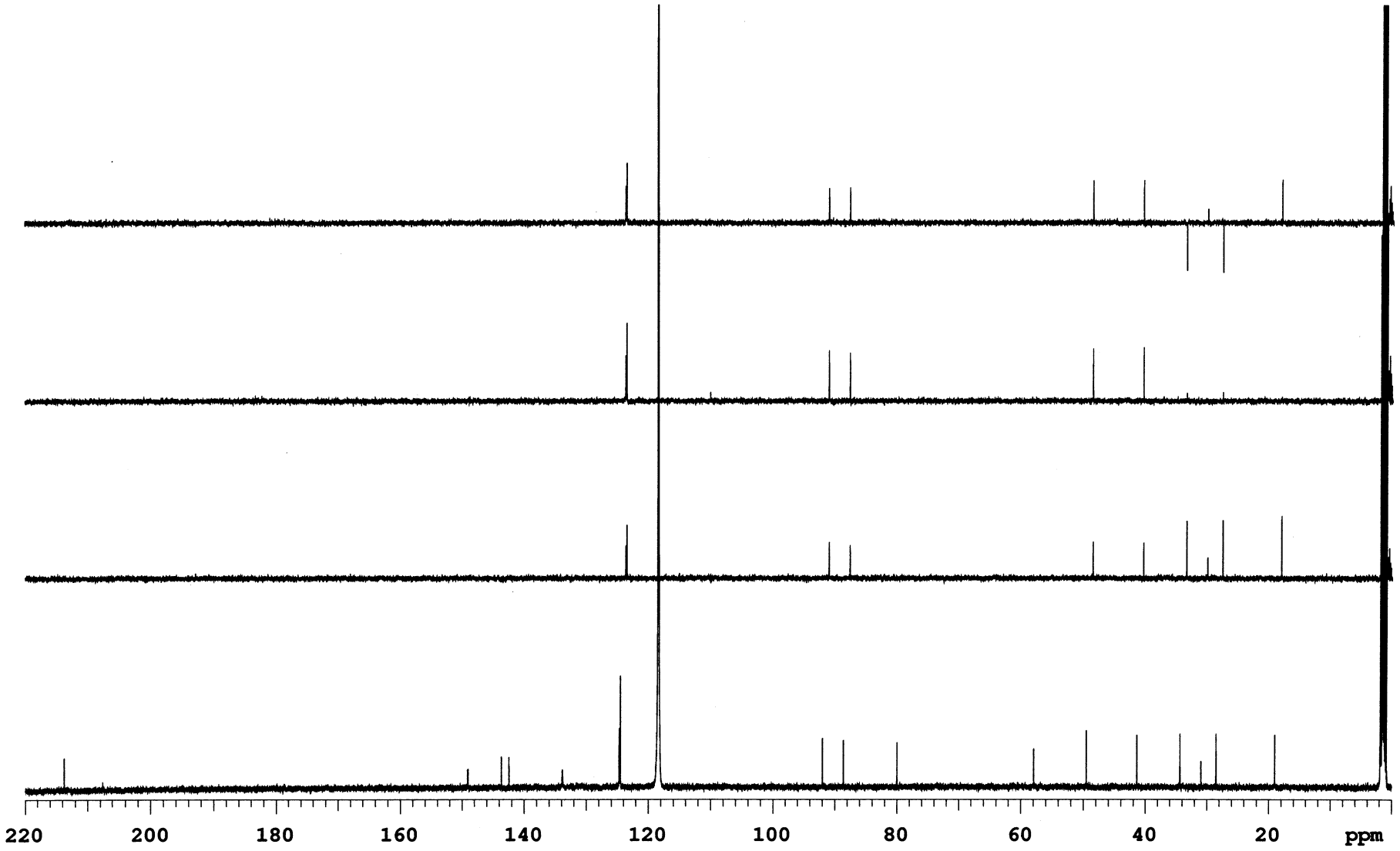


Fig S117. DEPT of compound 3h.

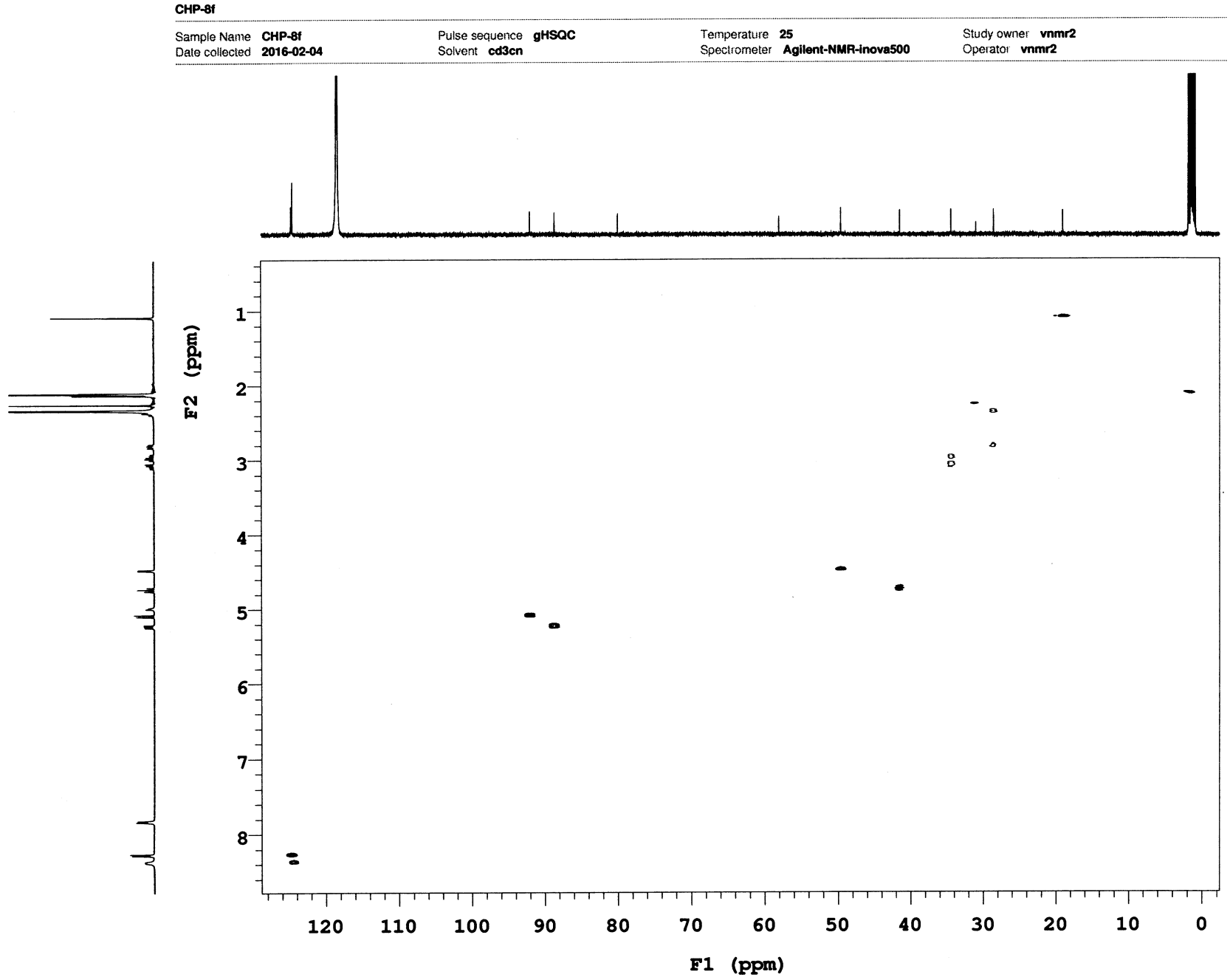


Fig S118. HSQC of compound 3h.

Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f/gHSQC_01

Plot date 2016-02-04

CHP-8f

Sample Name **CHP-8f** | Pulse sequence **gCOSY** | Temperature **25** | Study owner **vnmr2**
Date collected **2016-02-04** | Solvent **cd3cn** | Spectrometer **Agilent-NMR-inova500** | Operator **vnmr2**

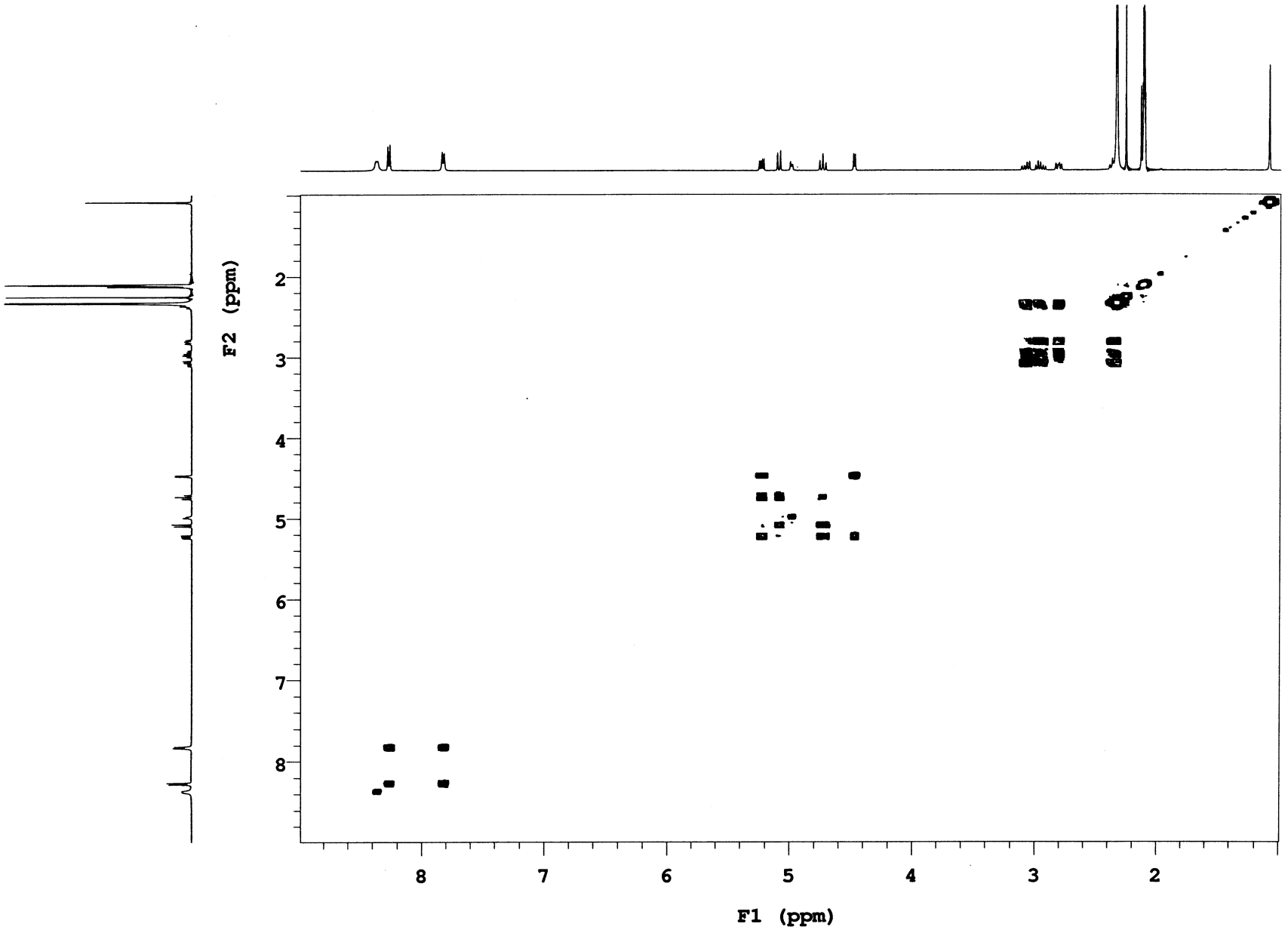


Fig S119. COSY of compound 3h.

Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f/gCOSY_01

Plot date 2016-02-04

CHP-8f

Sample Name **CHP-8f**	Pulse sequence **NOESY**	Temperature **25**	Study owner **vnmr2**
Date collected **2016-02-04**	Solvent **cd3cn**	Spectrometer **Agilent-NMR-inova500**	Operator **vnmr2**

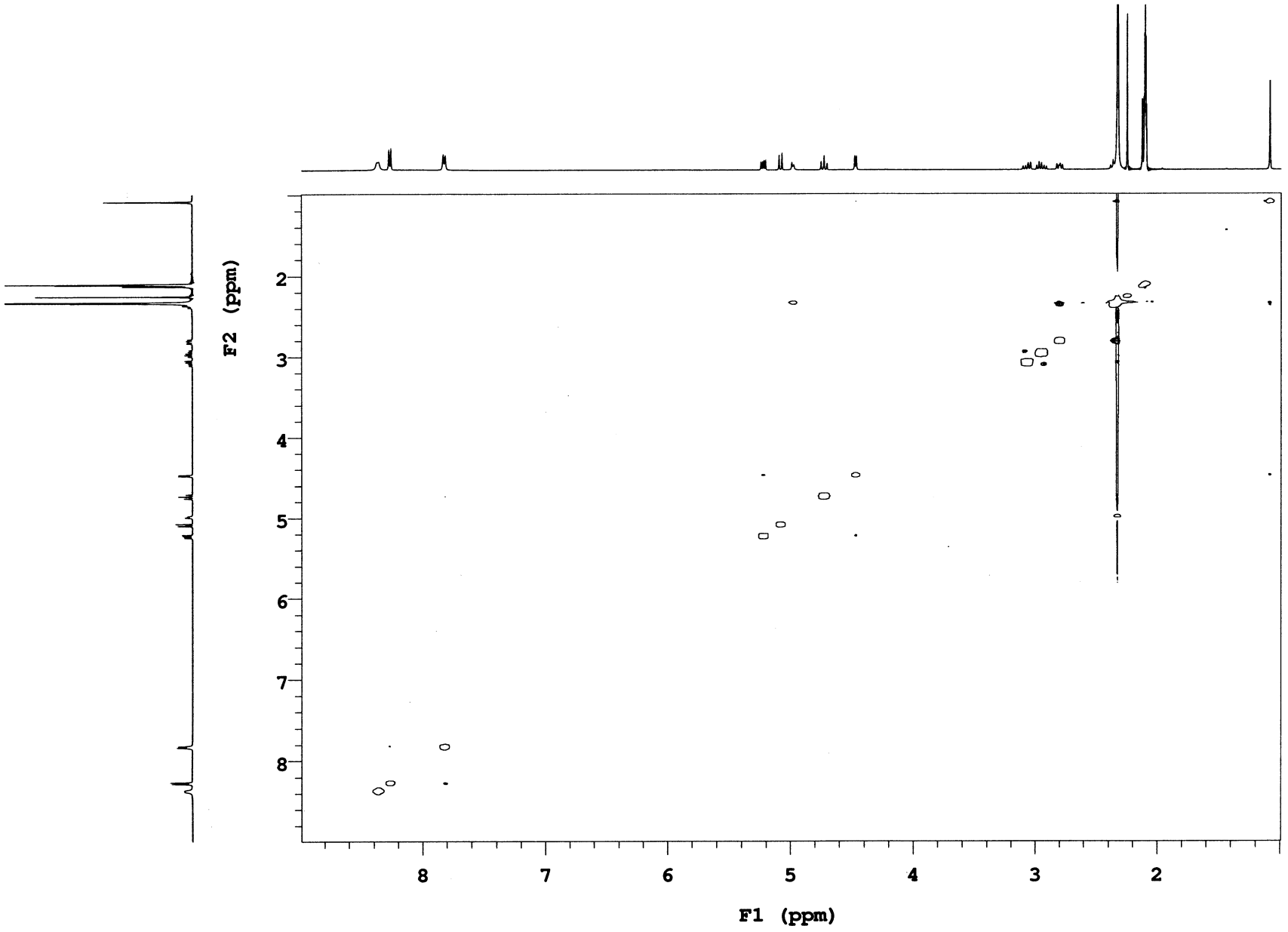
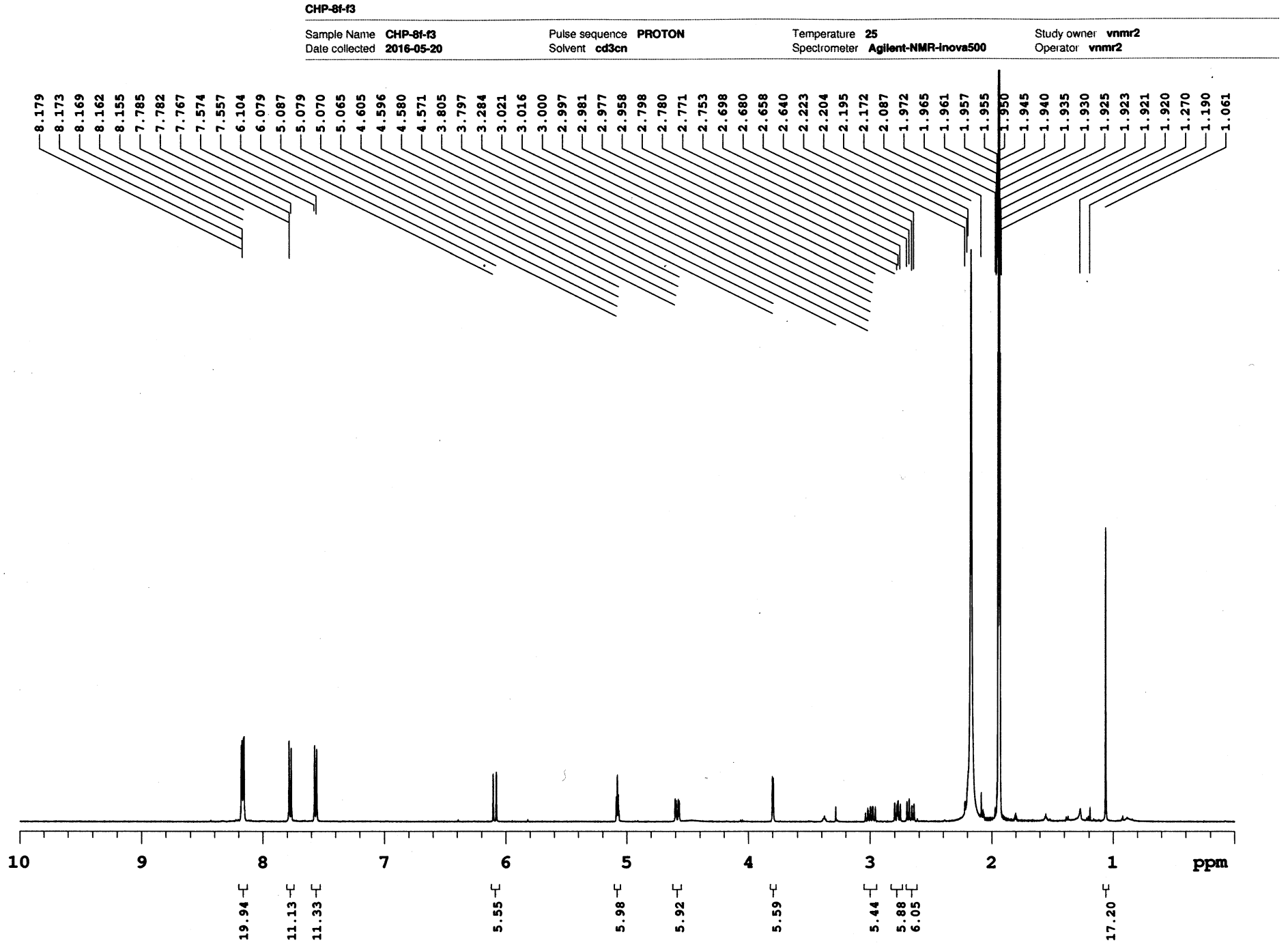


Fig S120. NOESY of compound 3h.

Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f/NOESY_01

Plot date 2016-02-04

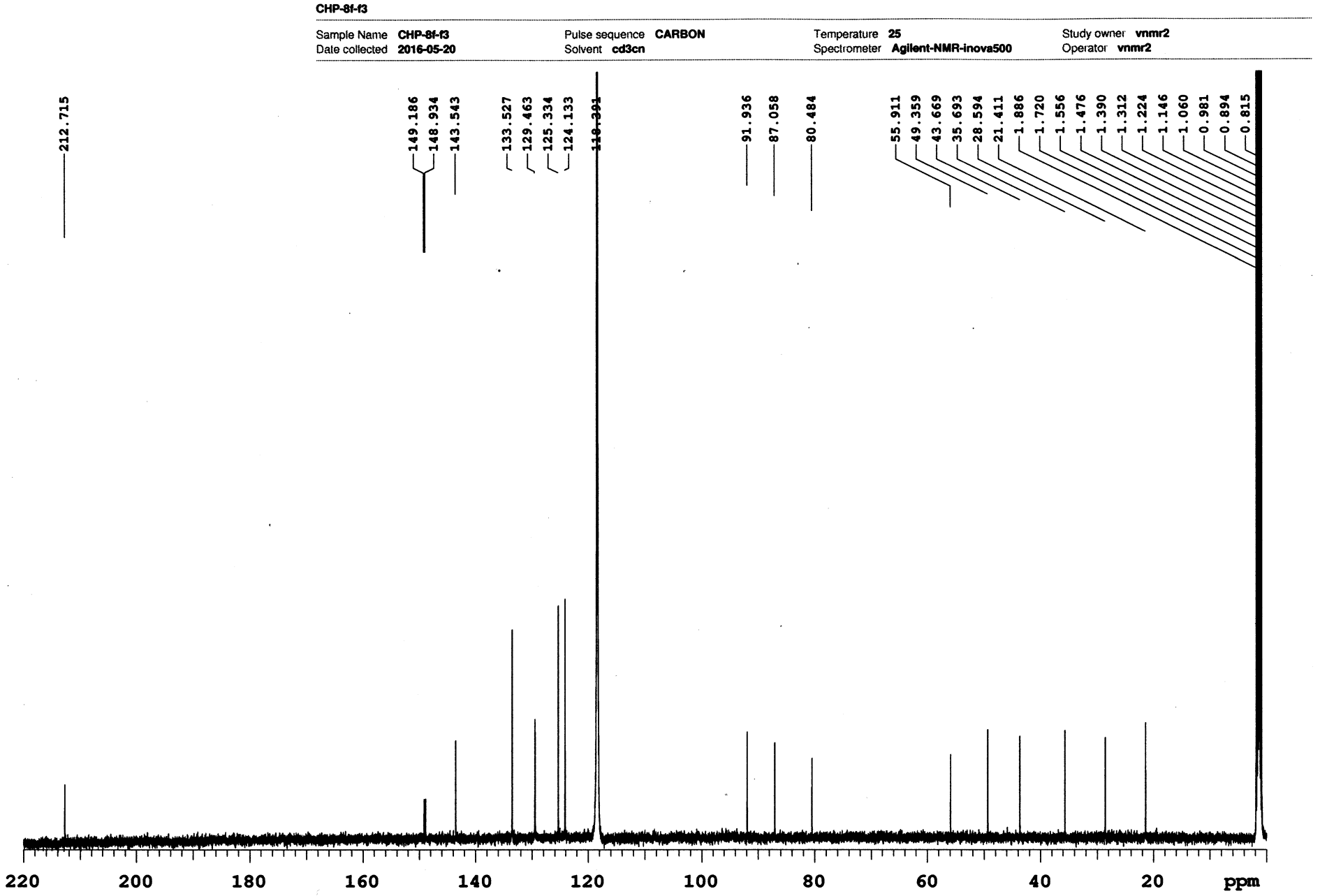
Fig S121. 1H NMR (CH3CN, 500 MHz) of compound 5h



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f-f3/PROTON_03

Plot date 2016-05-27

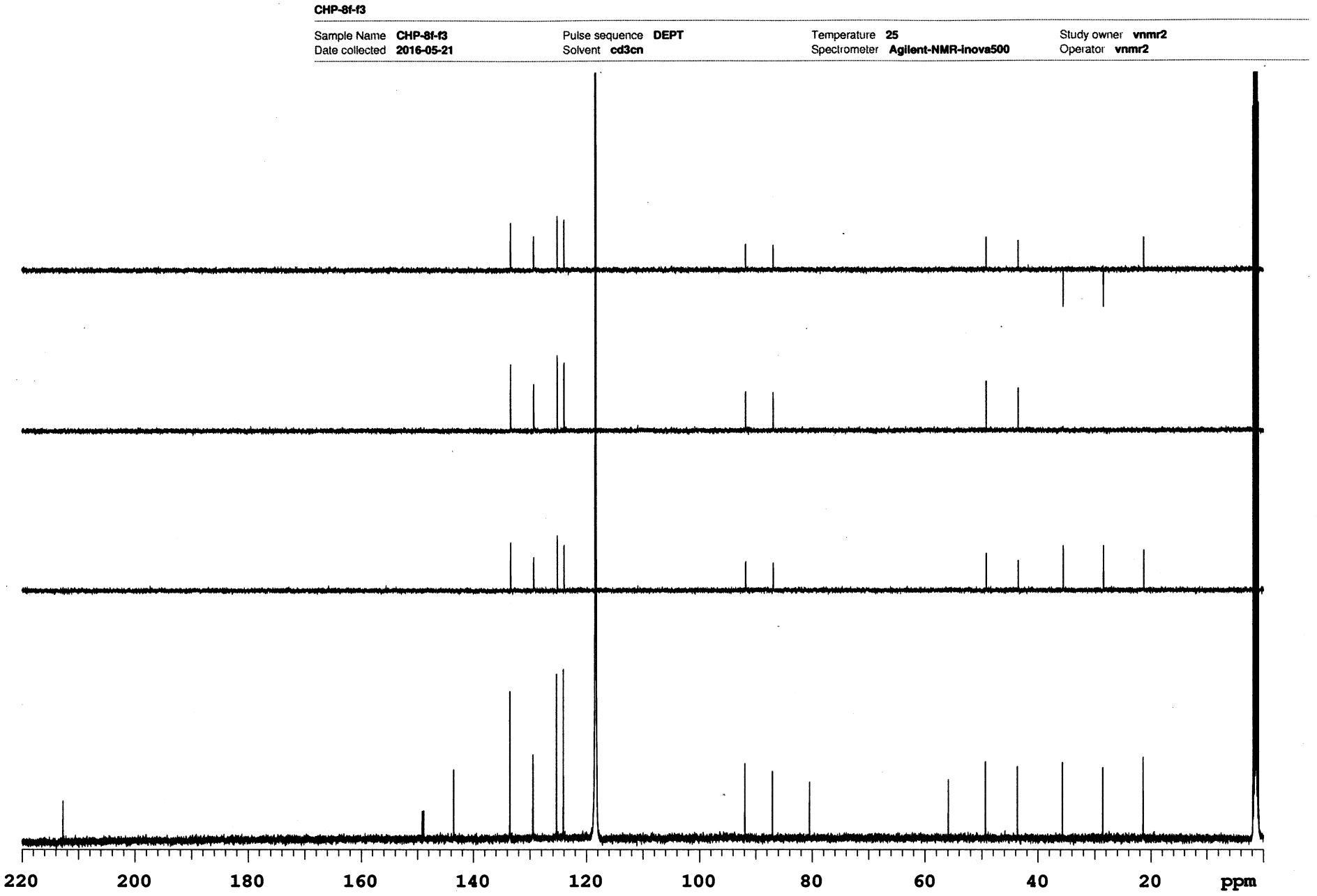
Fig S122. 13C NMR (CH3CN, 125 MHz) of compound 5h



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f-f3/CARBON_01

Plot date 2016-05-27

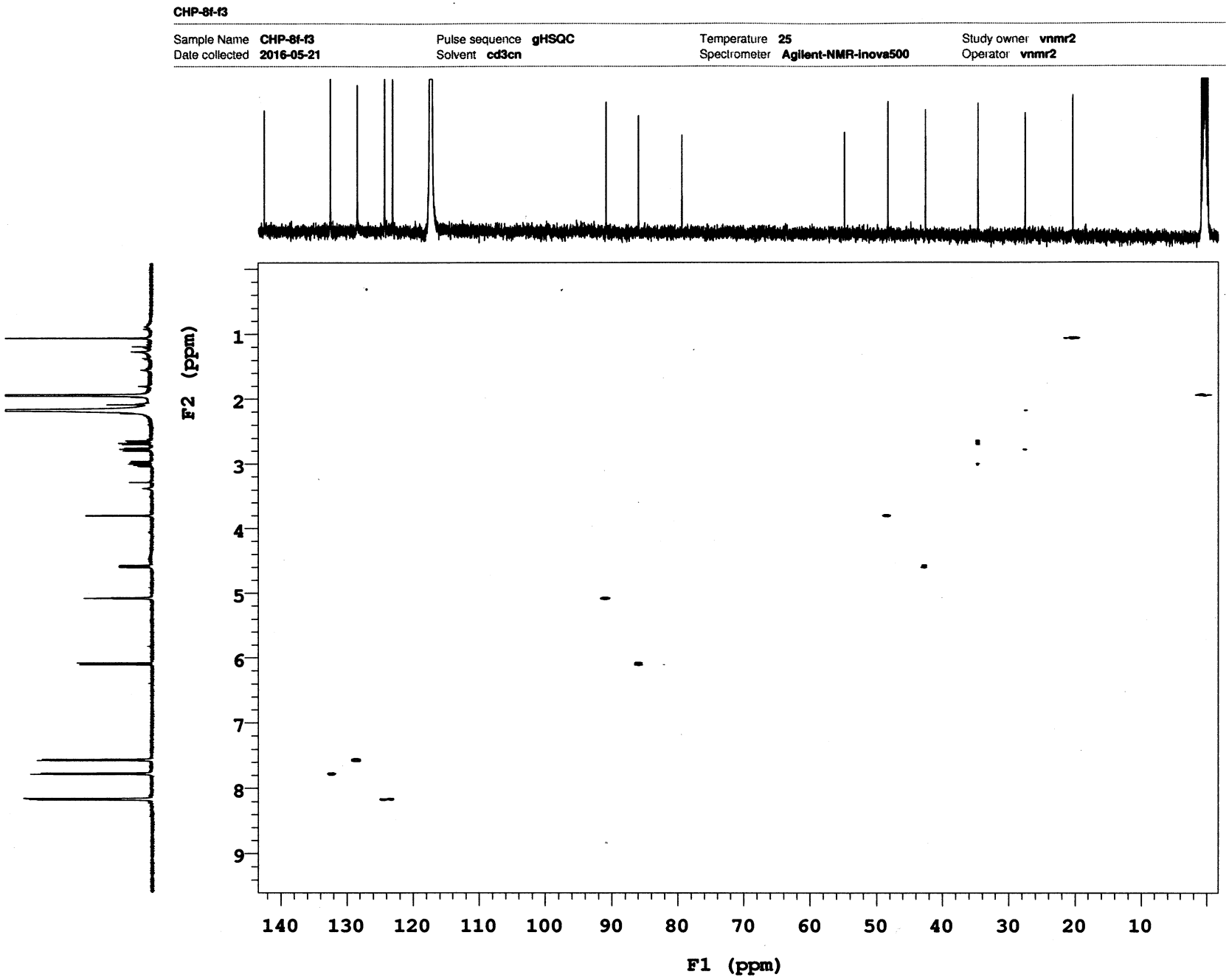
Fig S123. DEPT of compound 5h



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f-f3/DEPT_01.fid

Plot date 2016-05-27

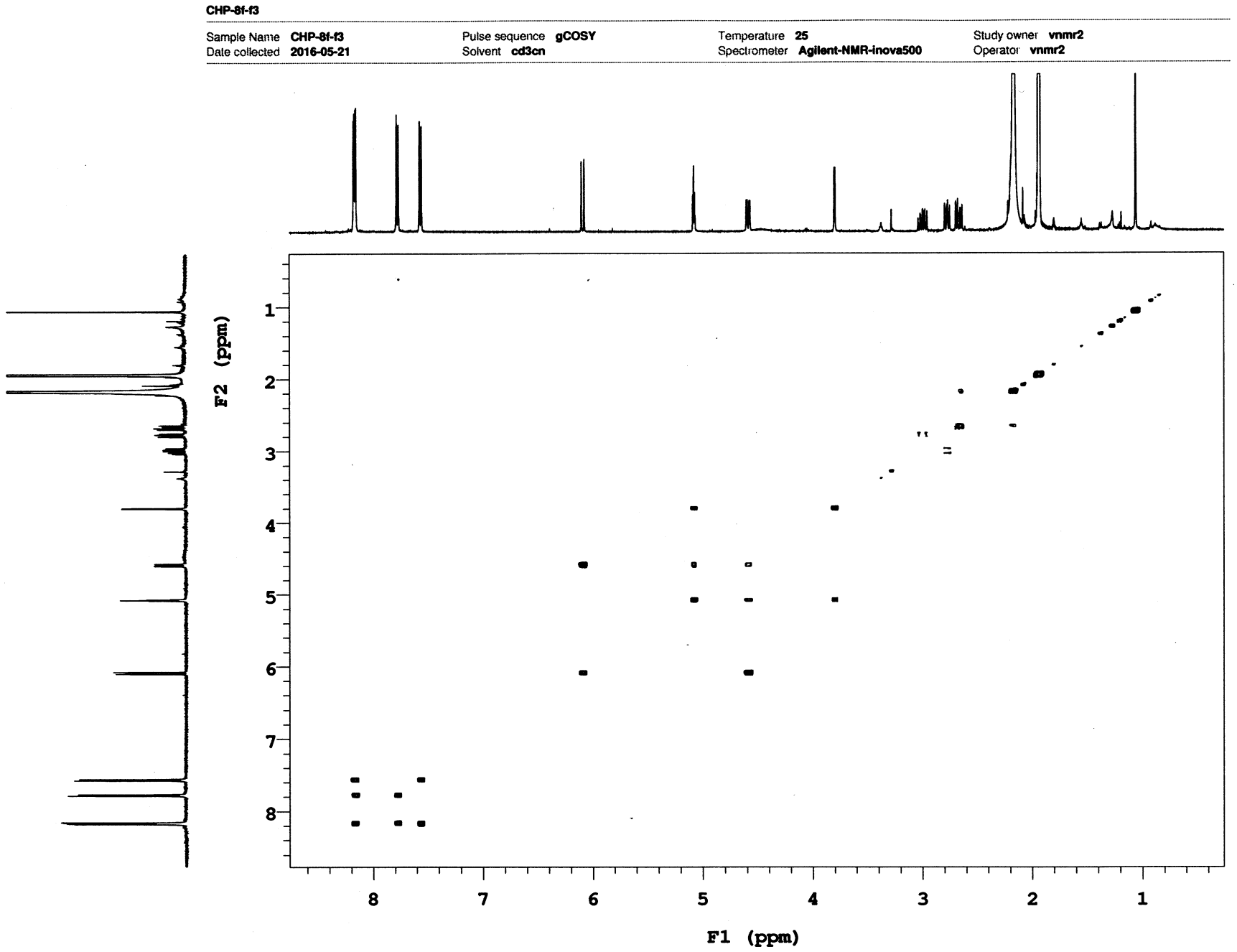
Fig S124. HSQC of compound 5h



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f-f3/gHSQC_01

Plot date 2016-05-27

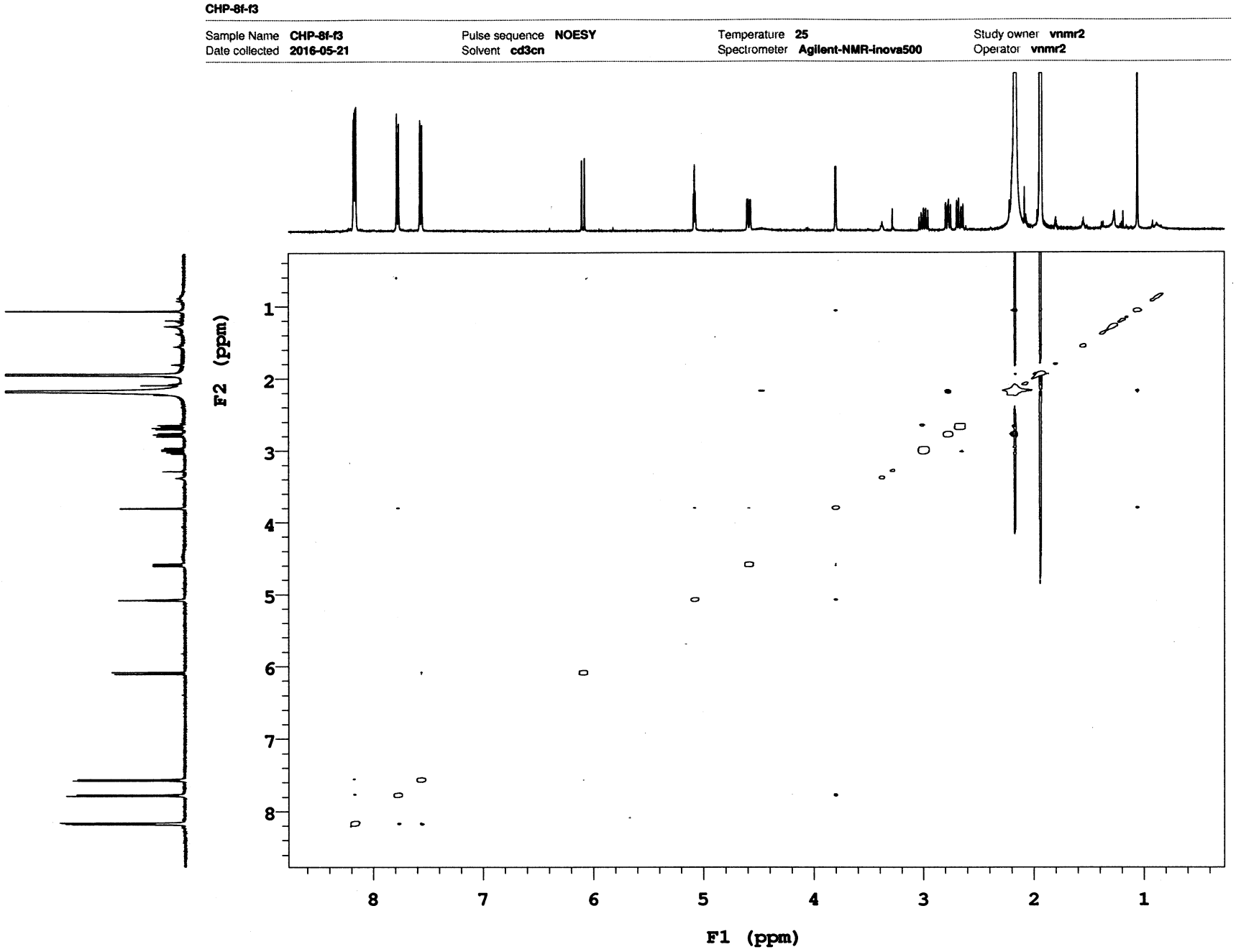
Fig S125. COSY of compound 5h



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f-f3/gCOSY_01

Plot date 2016-05-27

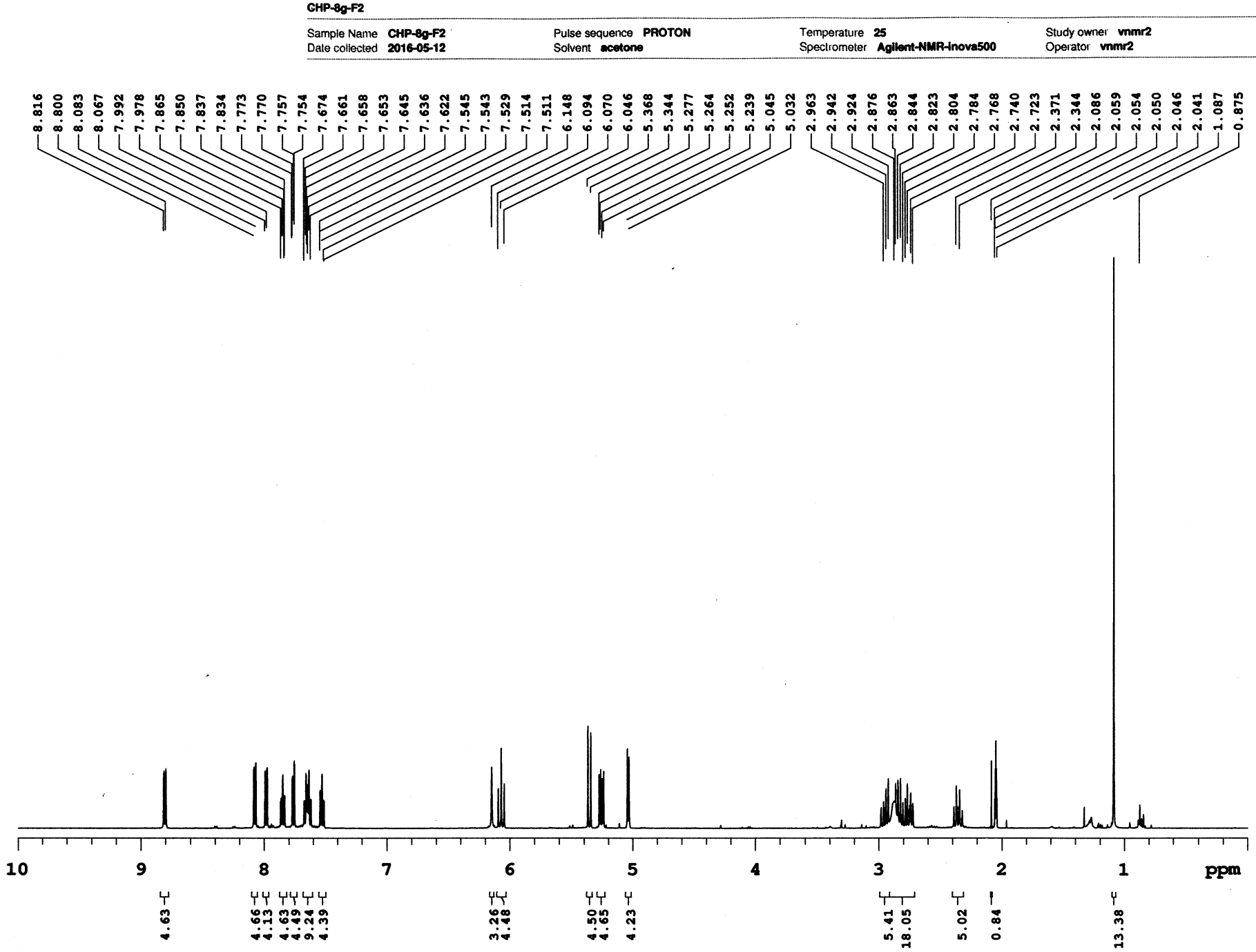
Fig S126. NOESY of compound 5h



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8f-f3/NOESY_01

Plot date 2016-05-27

Fig S127. 1H NMR (acetone-d6, 500 MHz) of compound 3i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g-F2/PROTON_05

Plot date 2016-05-12

Fig S128. 13C NMR (acetone-d6, 125 MHz) of compound 3i.

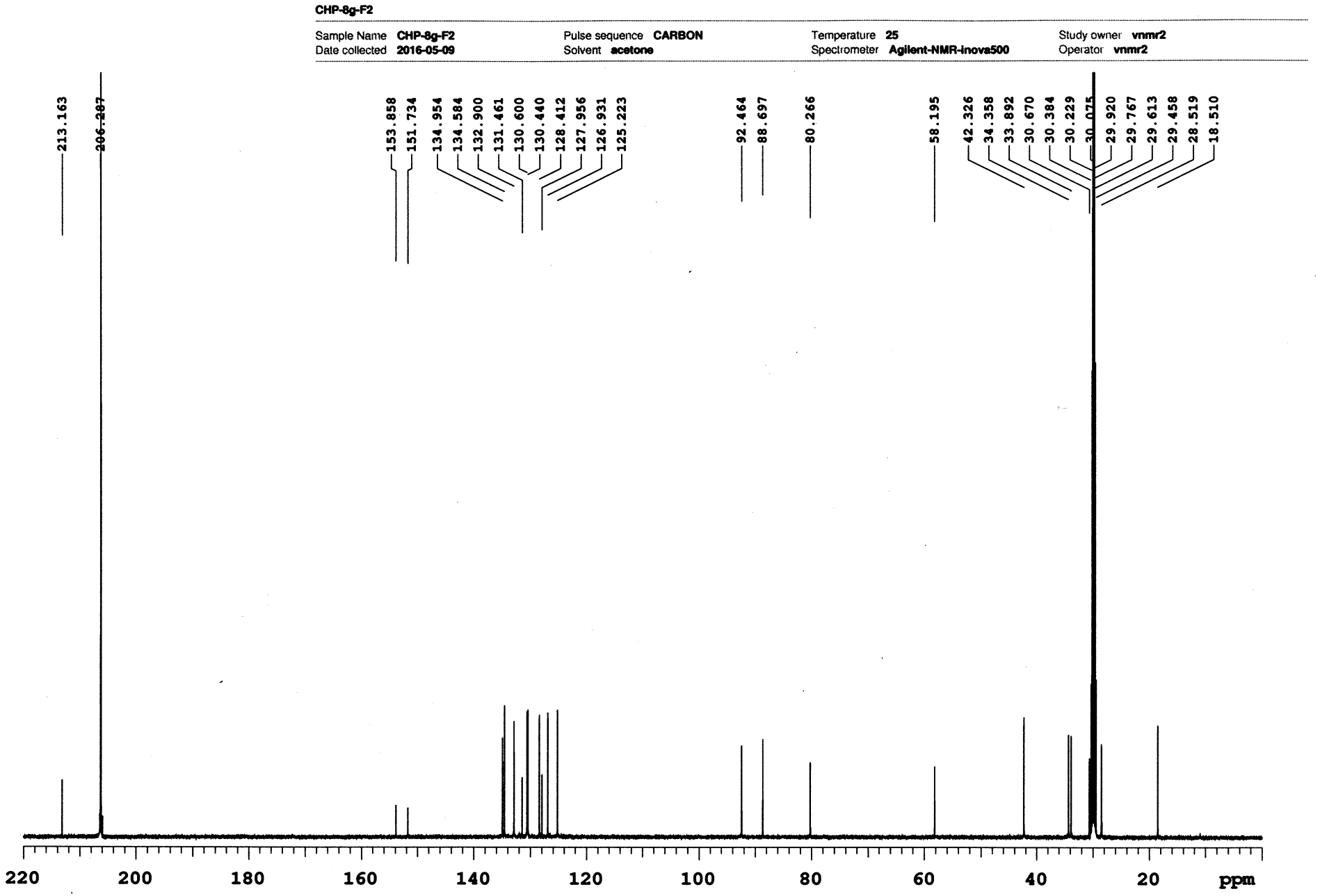
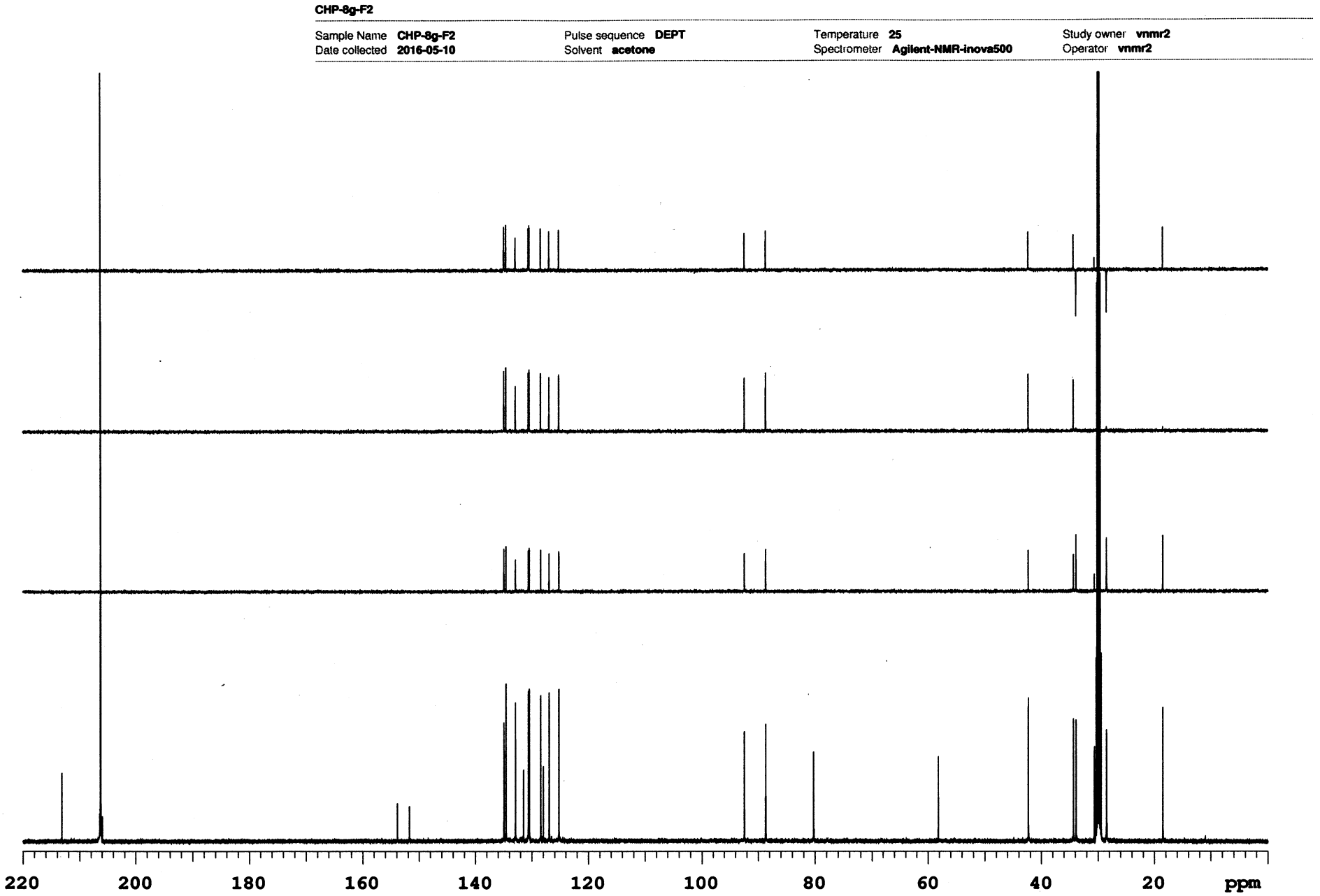


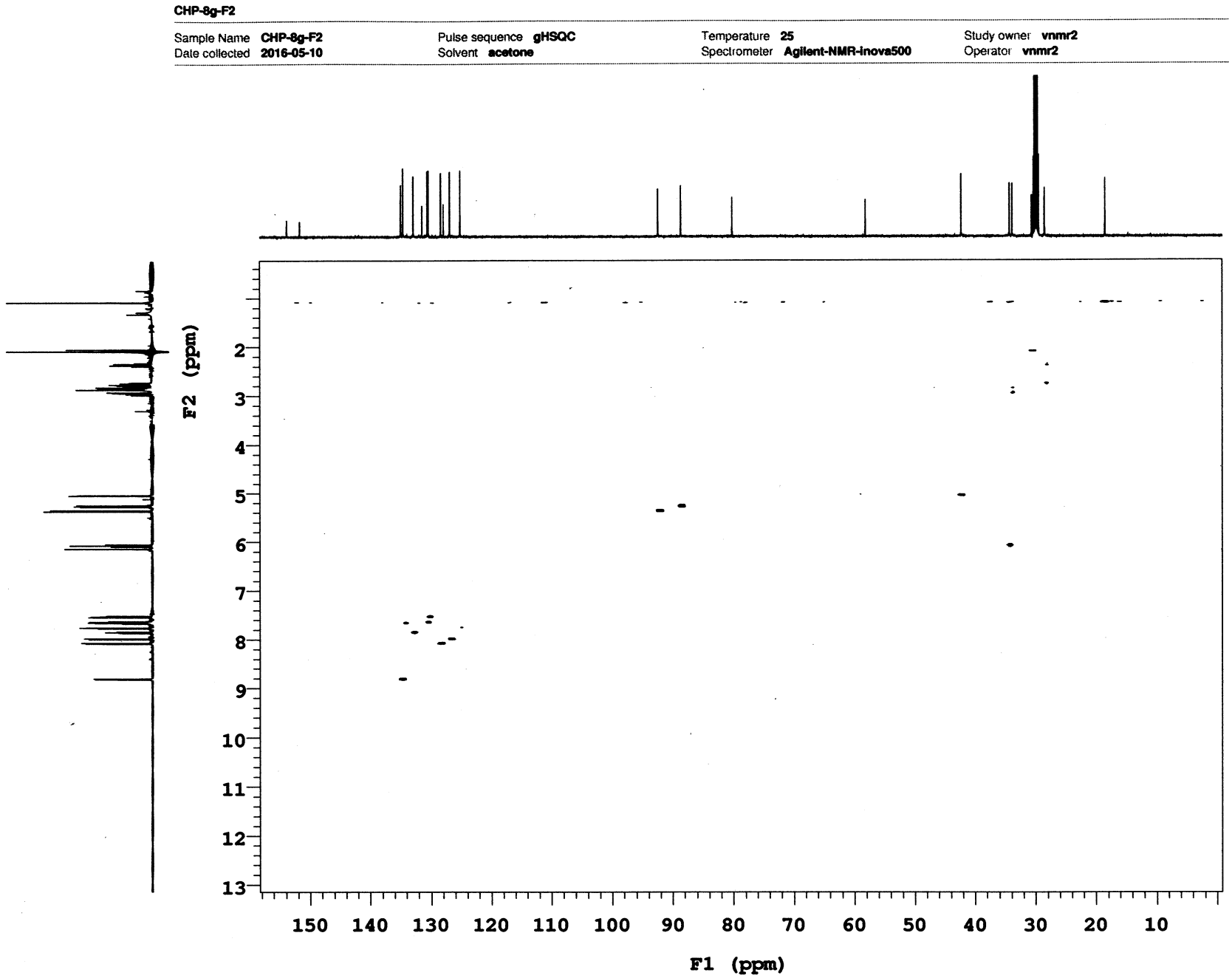
Fig S129. DEPT (acetone-d6) of compound 3i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g-F2/DEPT_01

Plot date 2016-05-10

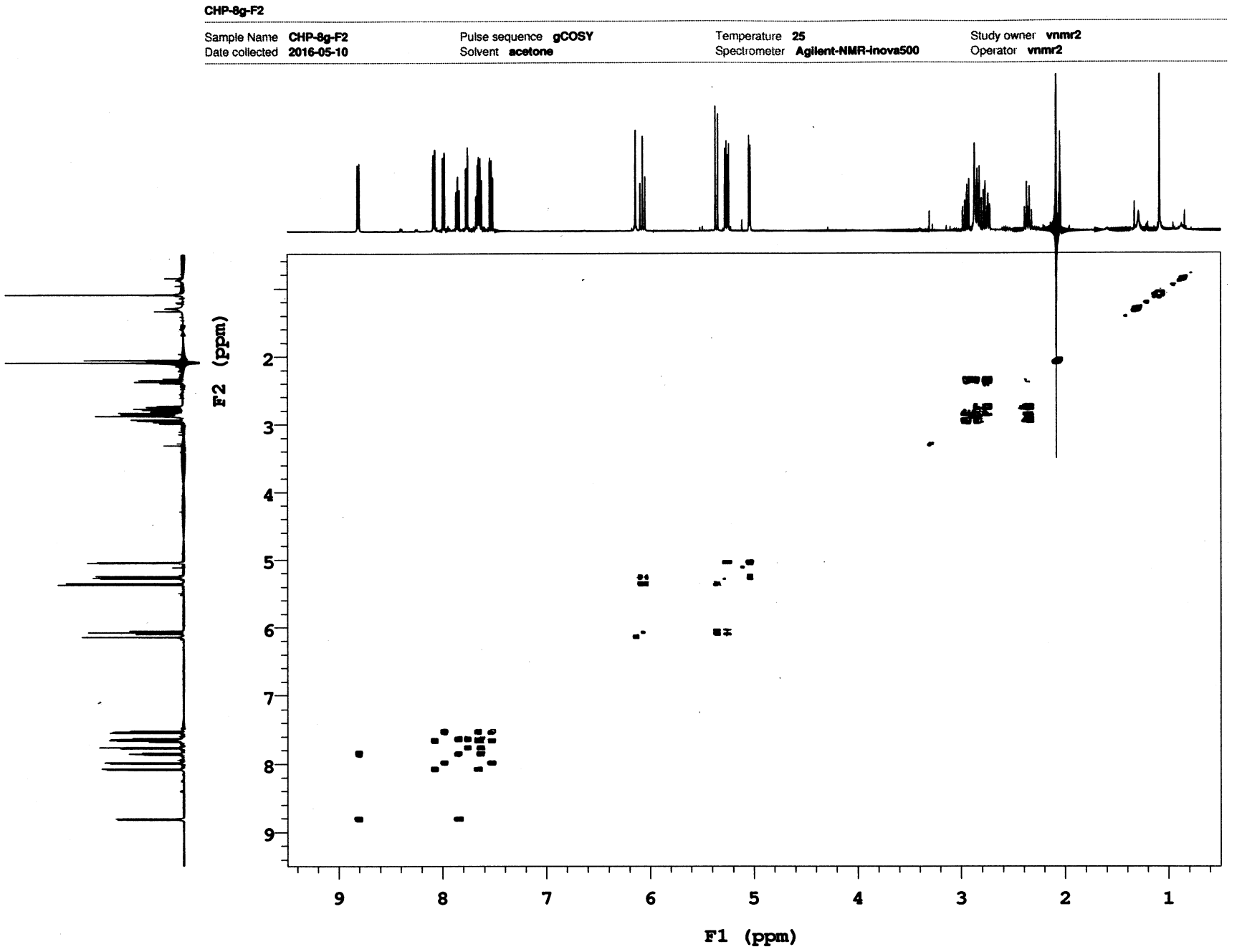
Fig S130. HSQC (acetone-d6) of compound 3i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g-F2/gHSQC_02

Plot date 2016-05-10

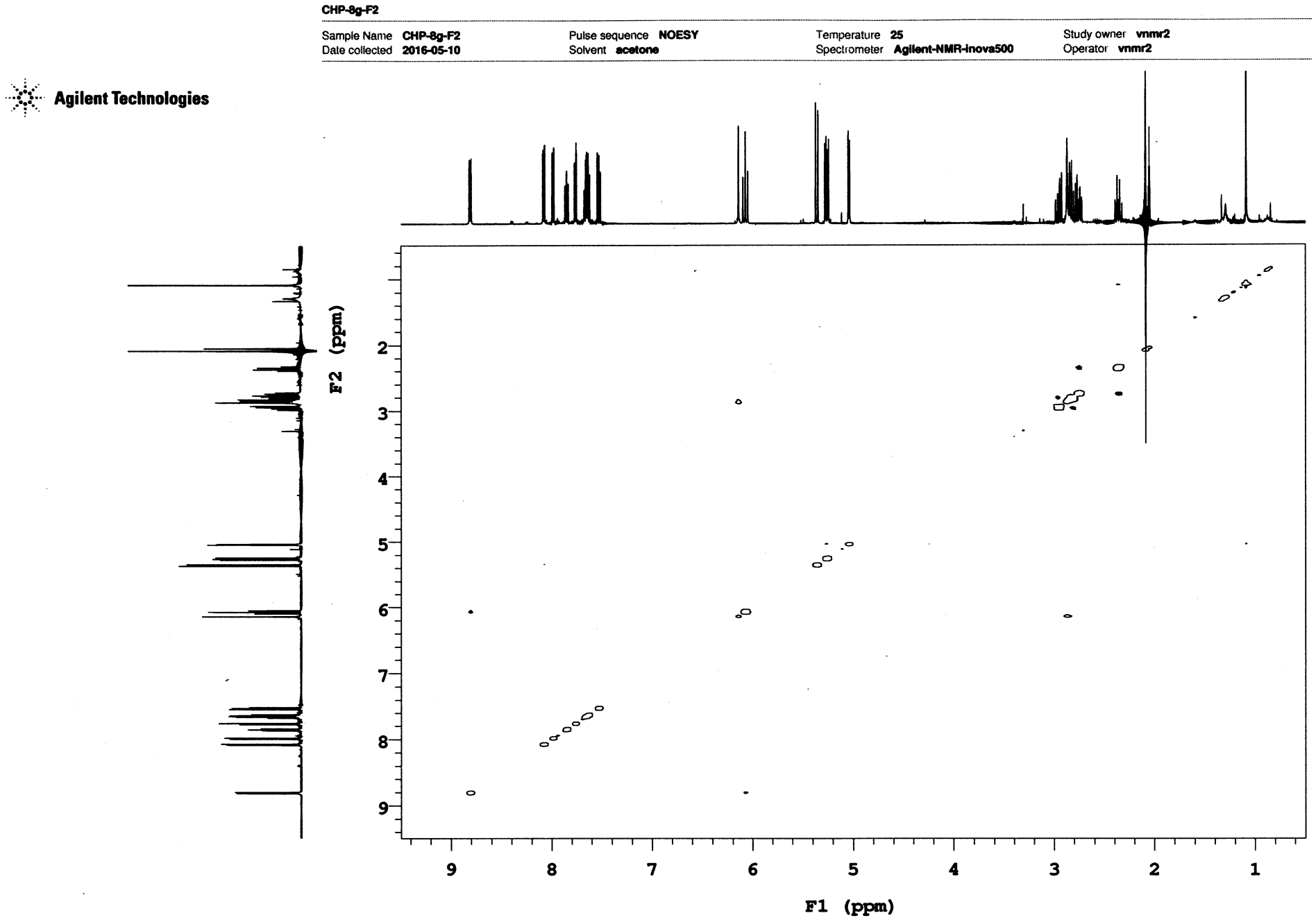
Fig S131. COSY (acetone-d6) of compound 3i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g-F2/gCOSY_01

Plot date 2016-05-10

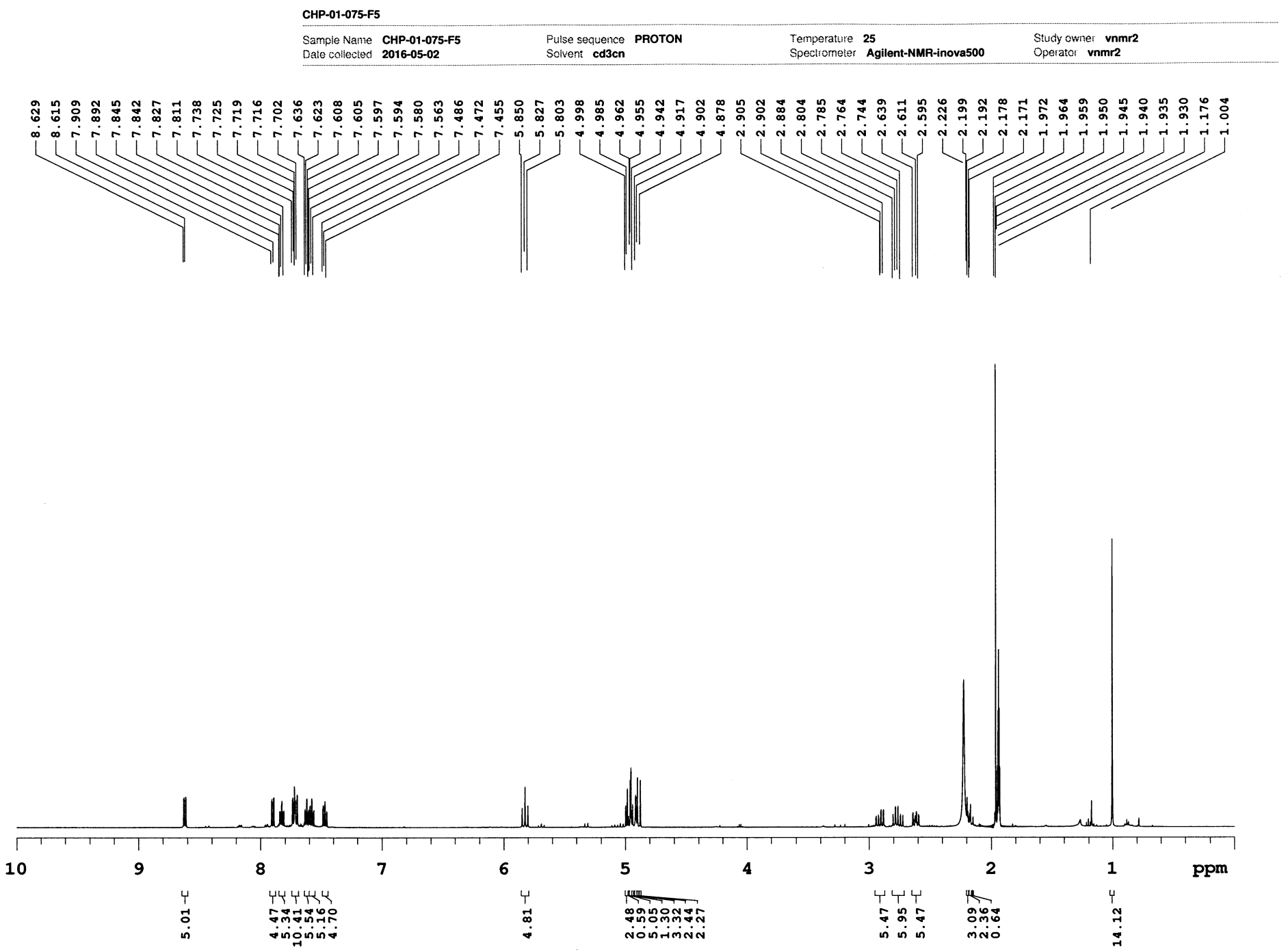
Fig S132. NOESY (acetone-d6) of compound 3i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g-F2/NOESY_01

Plot date 2016-05-10

Fig S133. 1H NMR (CD3CN, 500 MHz) of compound 3i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-01-075-F5/PROTON_04

Plot date 2016-05-05

Fig S134. 13C NMR (CD3CN, 125 MHz) of compound 3i.

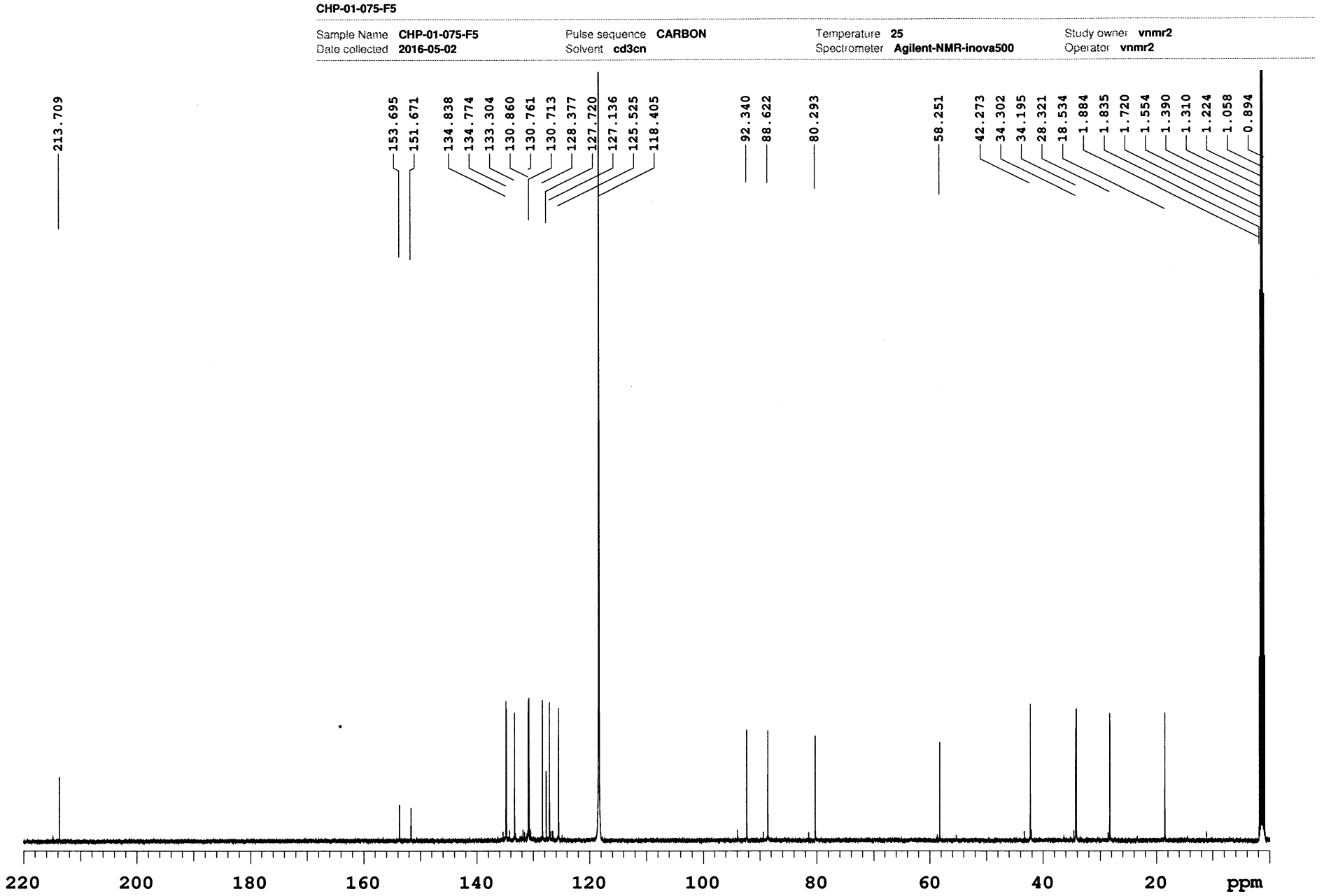
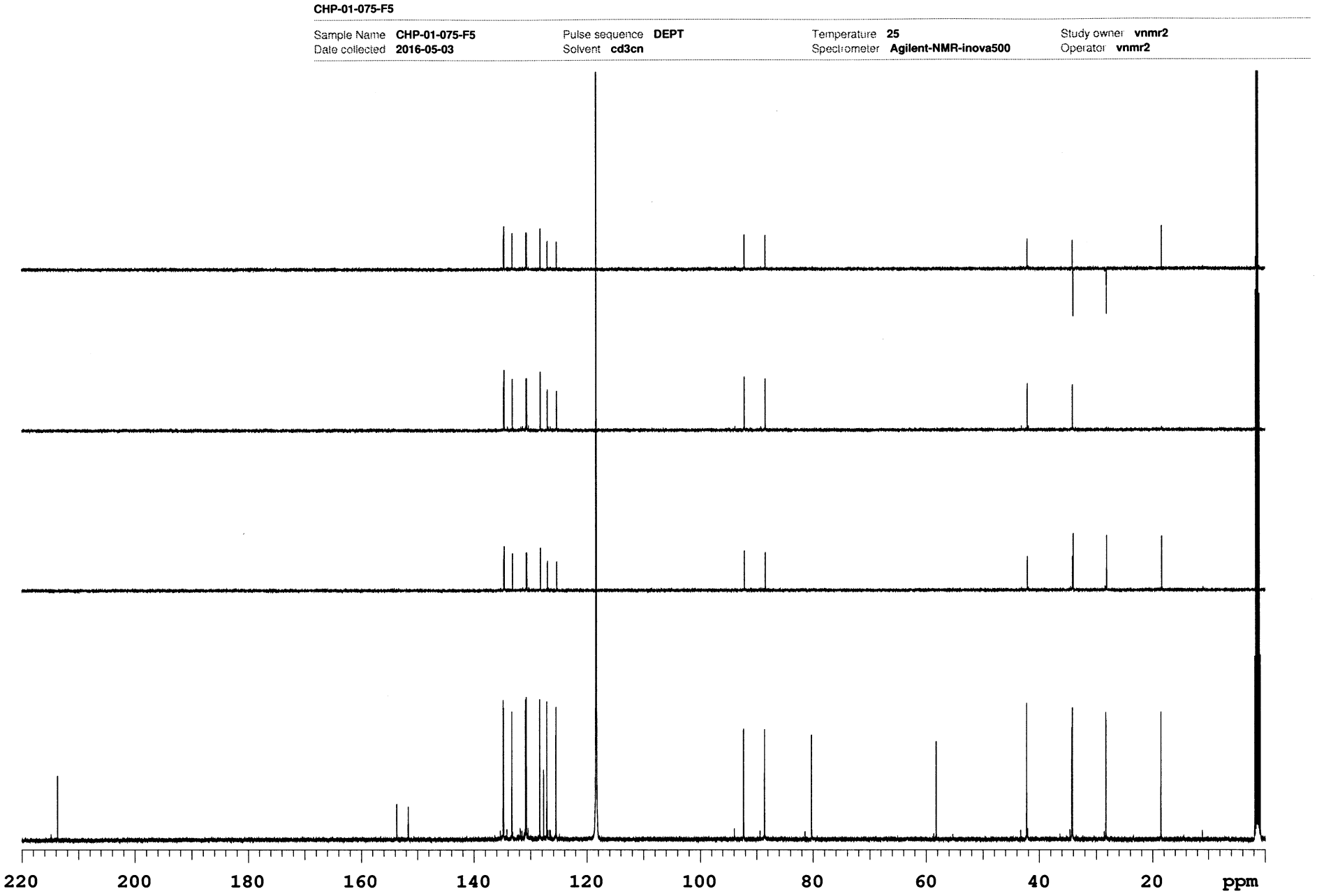


Fig S135. DEPT (CD3CN) of compound 3i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-01-075-F5/DEPT_01

Plot date 2016-05-03

Fig S136. HSQC (CD3CN) of compound 3i.

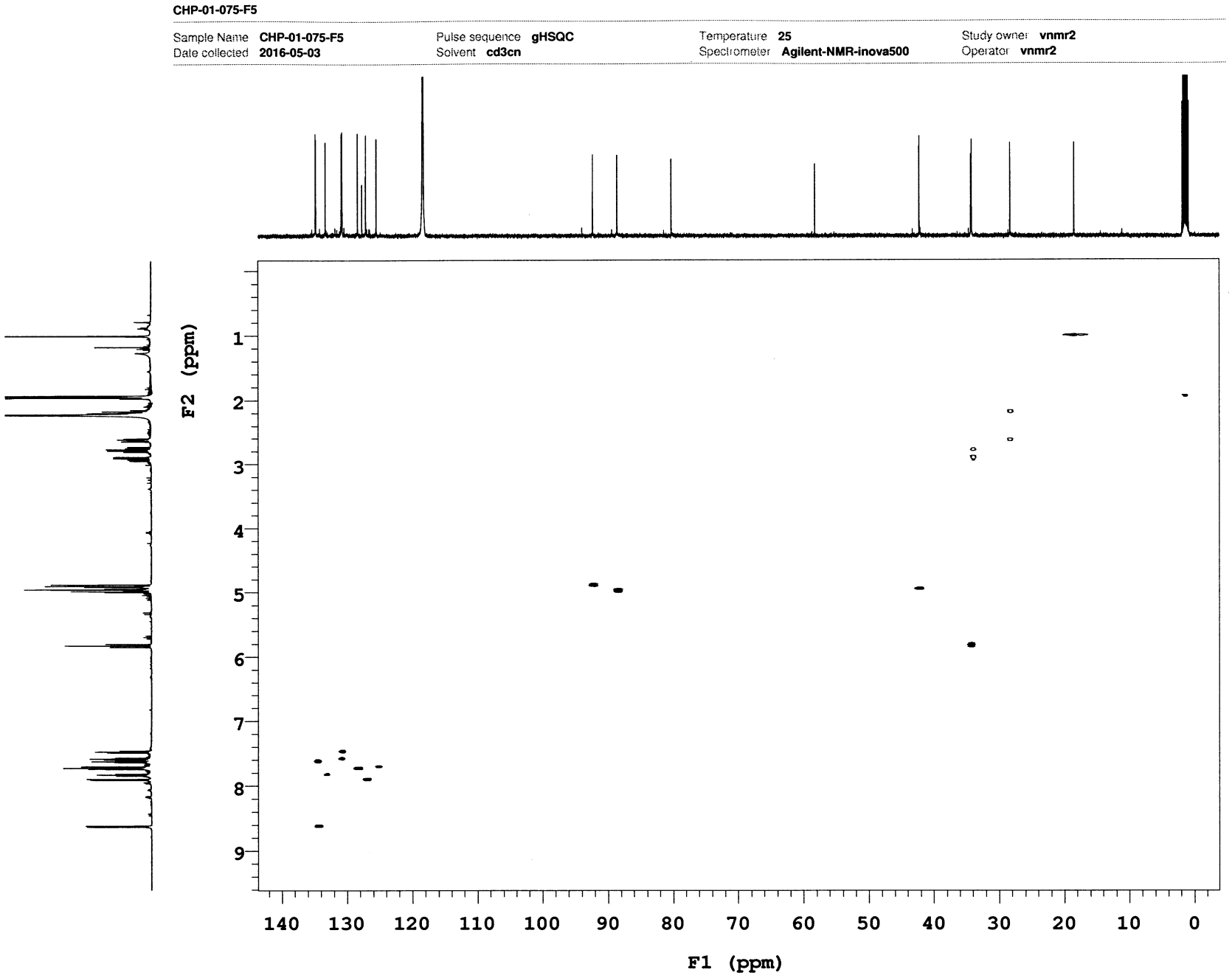
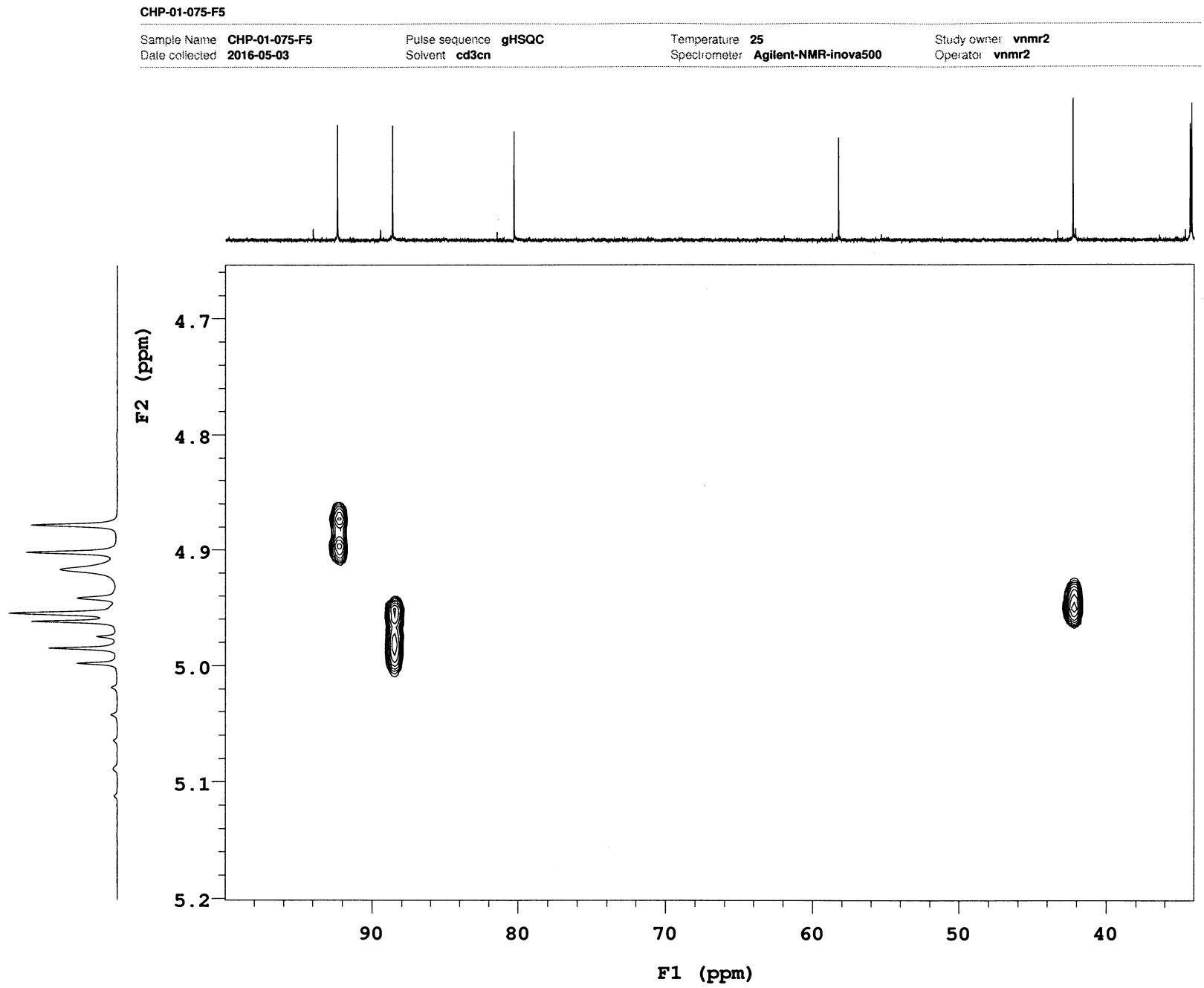


Fig S137. HSQC (CD3CN) of compound 3i, expand.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-01-075-F5/gHSQC_01

Plot date 2016-05-05

Fig S138. COSY (CD3CN) of compound 3i.

CHP-01-075-F5

Sample Name	CHP-01-075-F5	Pulse sequence	gCOSY	Temperature	25	Study owner	vnmr2
Date collected	2016-05-03	Solvent	cd3cn	Spectrometer	Agilent-NMR-inova500	Operator	vnmr2

Agilent Technologies

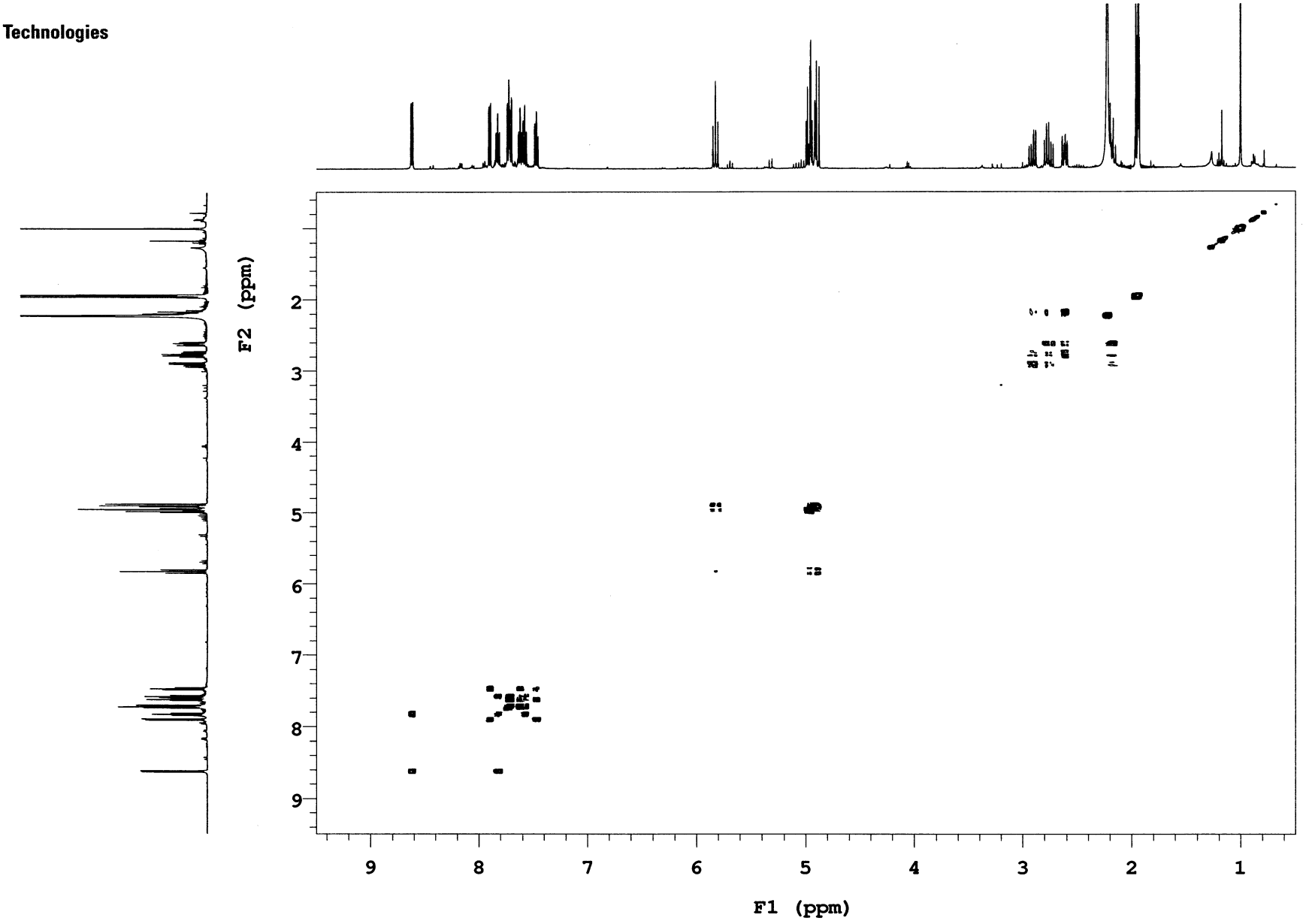
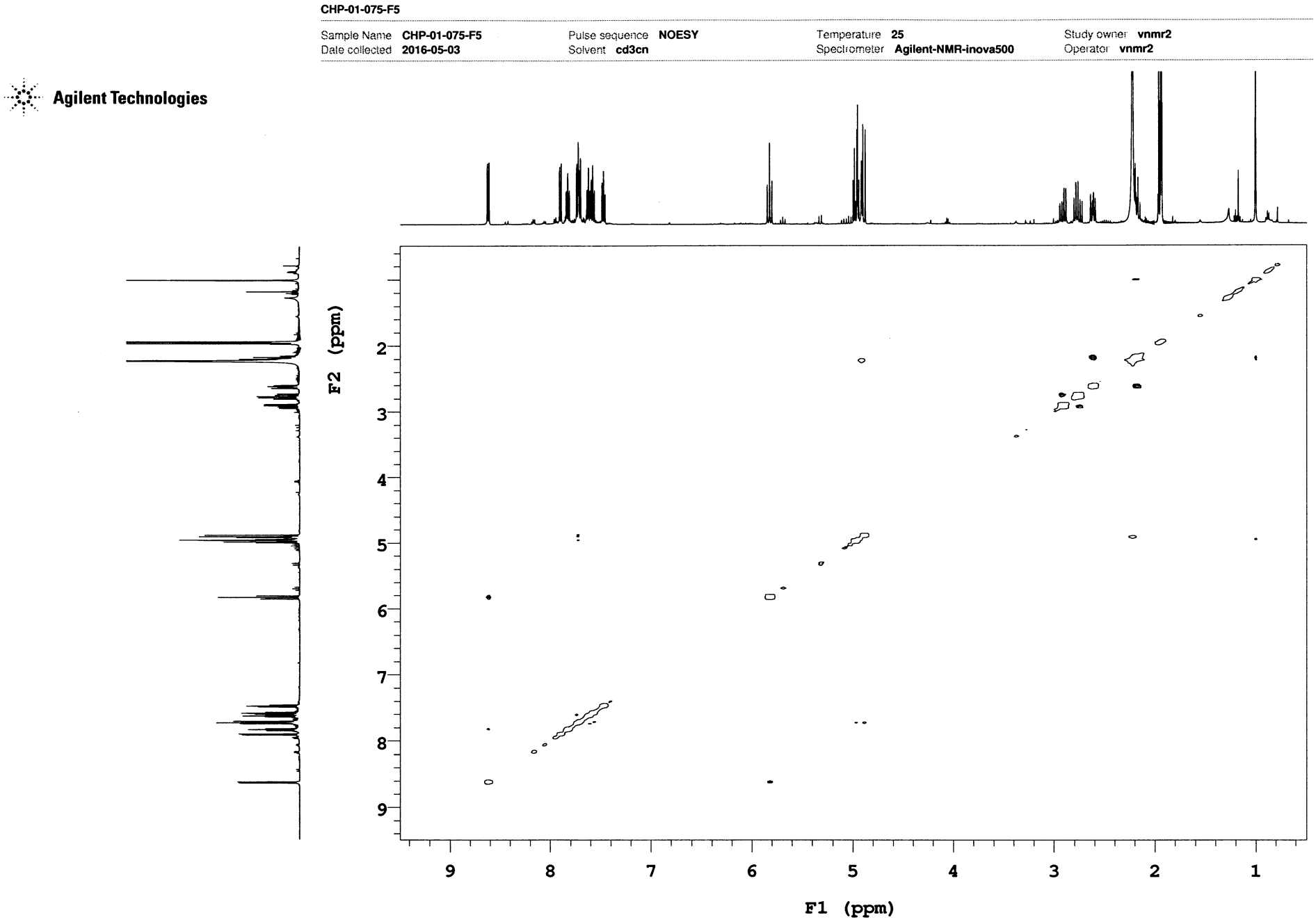


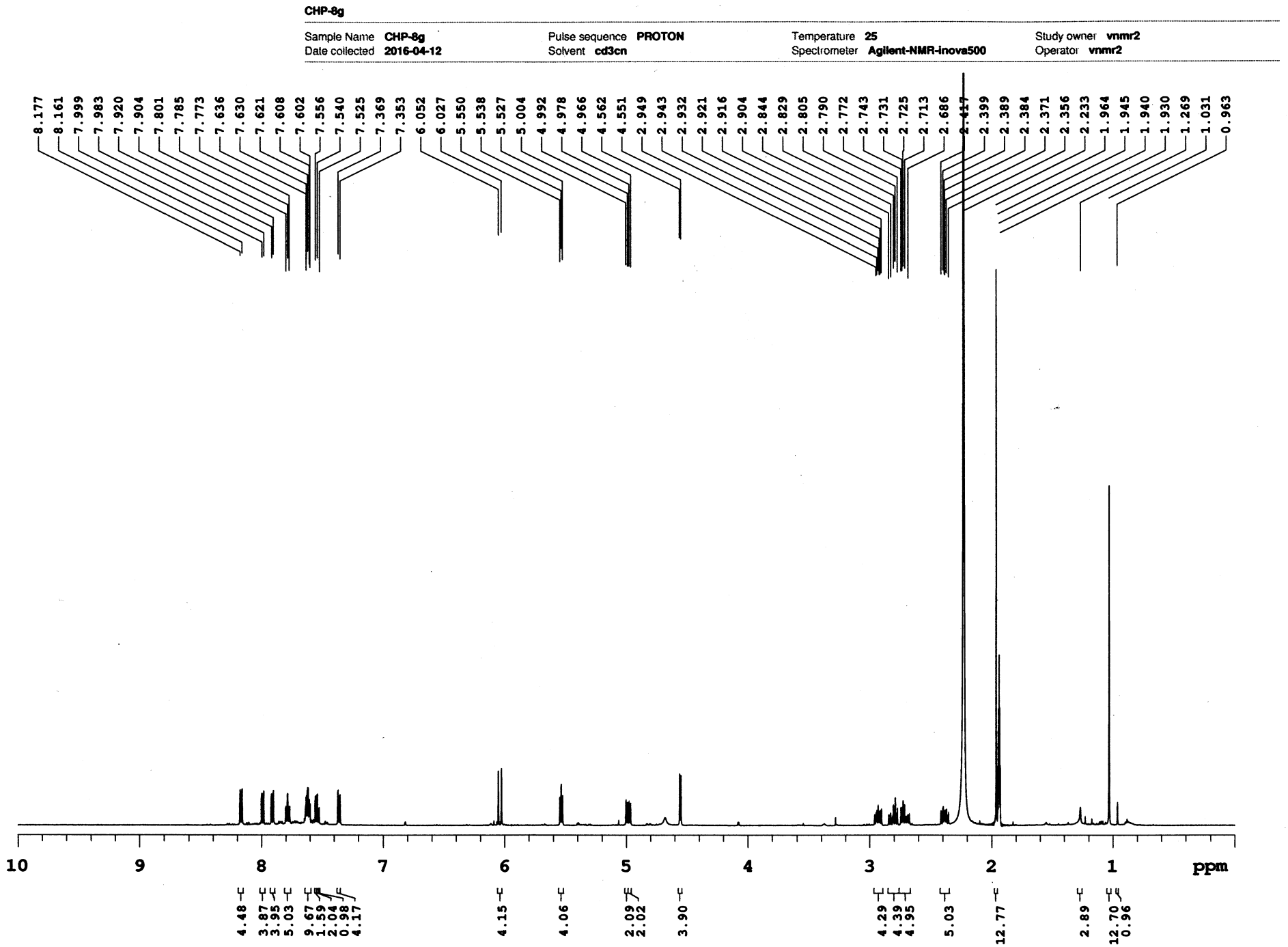
Fig S139. NOESY (CD3CN) of compound 3i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-01-075-F5/NOESY_01

Plot date 2016-05-03

Fig S140. 1H NMR (CD3CN, 500 MHz) of compound 5i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g/PROTON_05

Plot date 2016-04-15

Fig S141. 13C NMR (CD3CN, 125 MHz) of compound 5i.

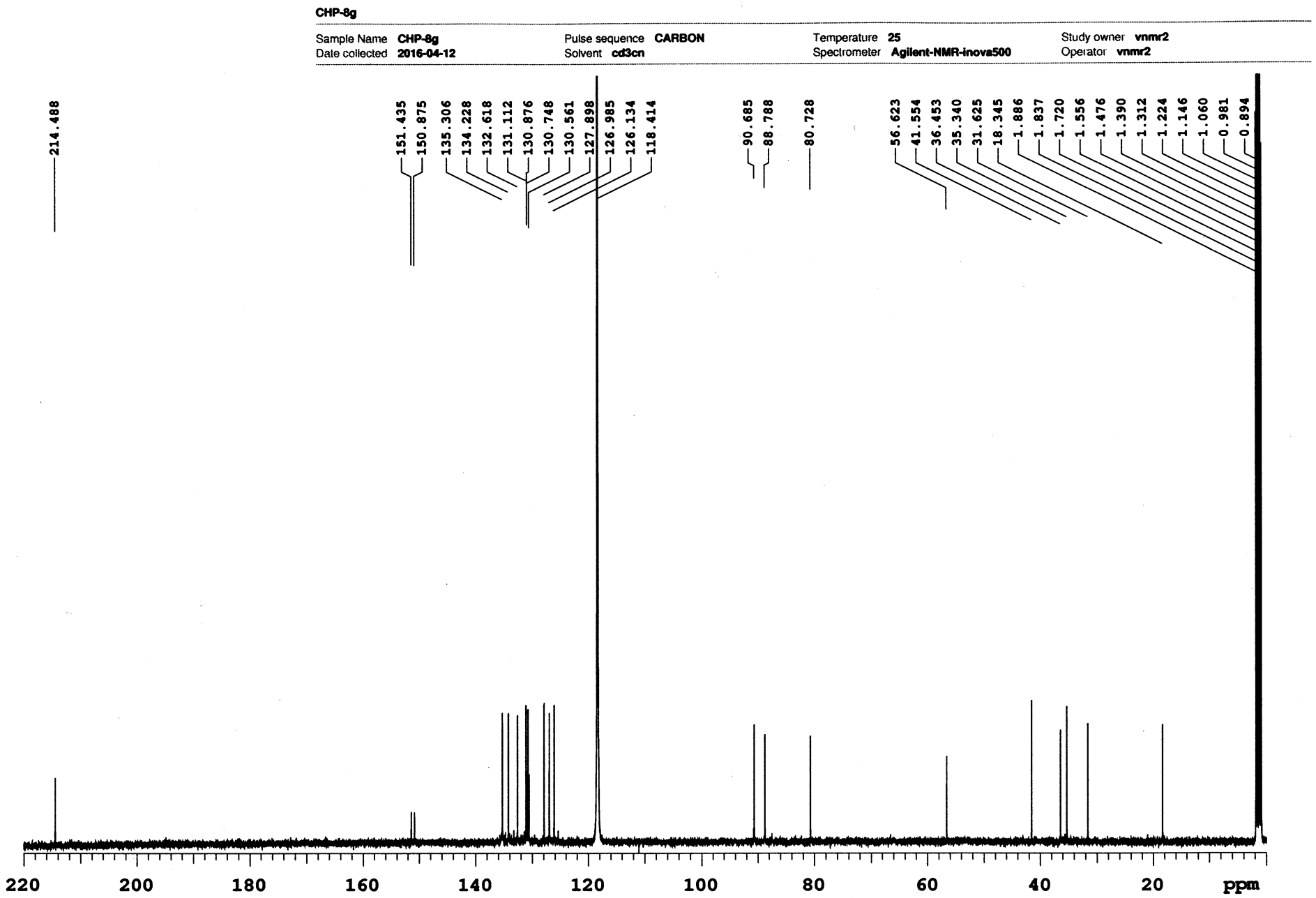
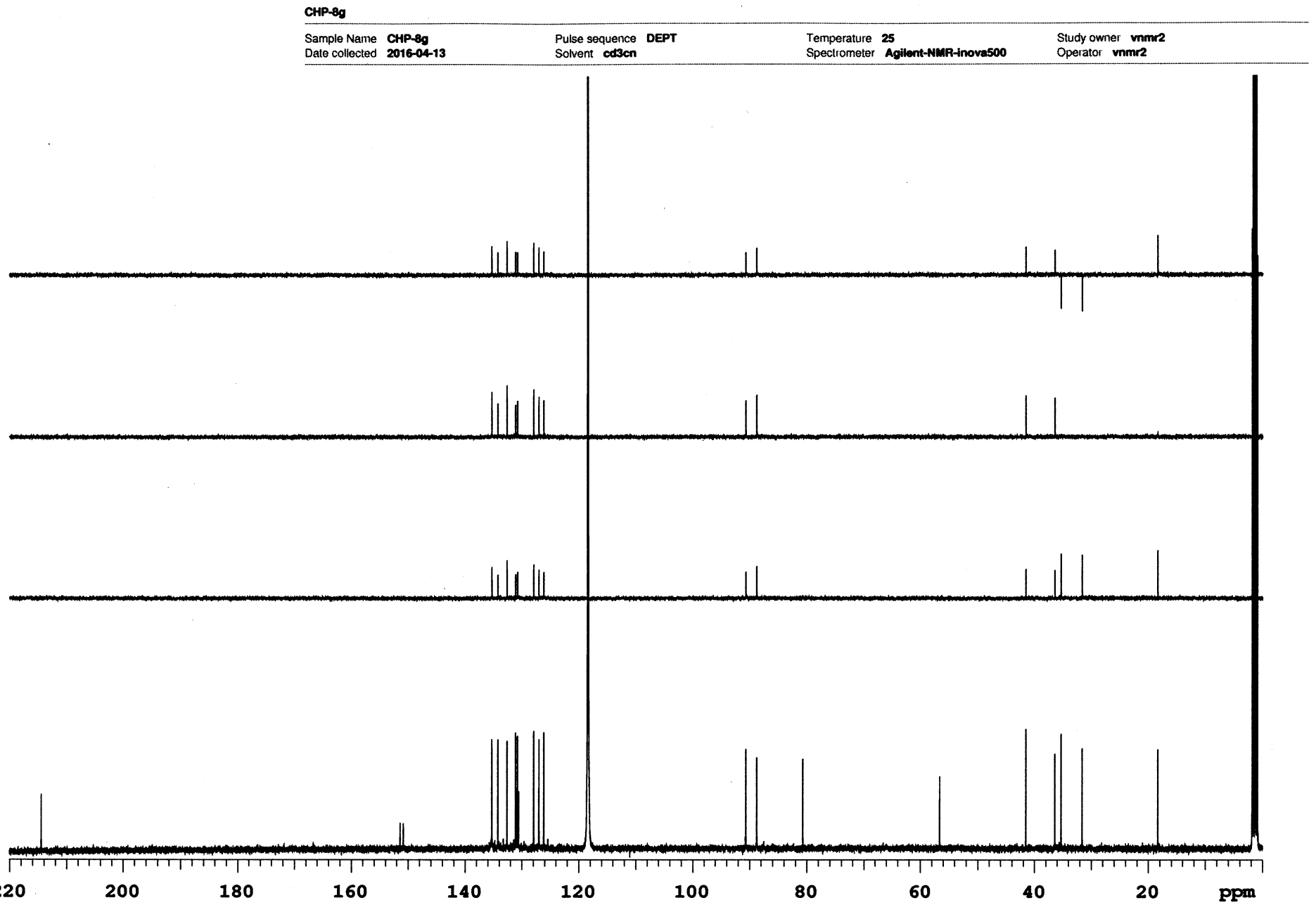


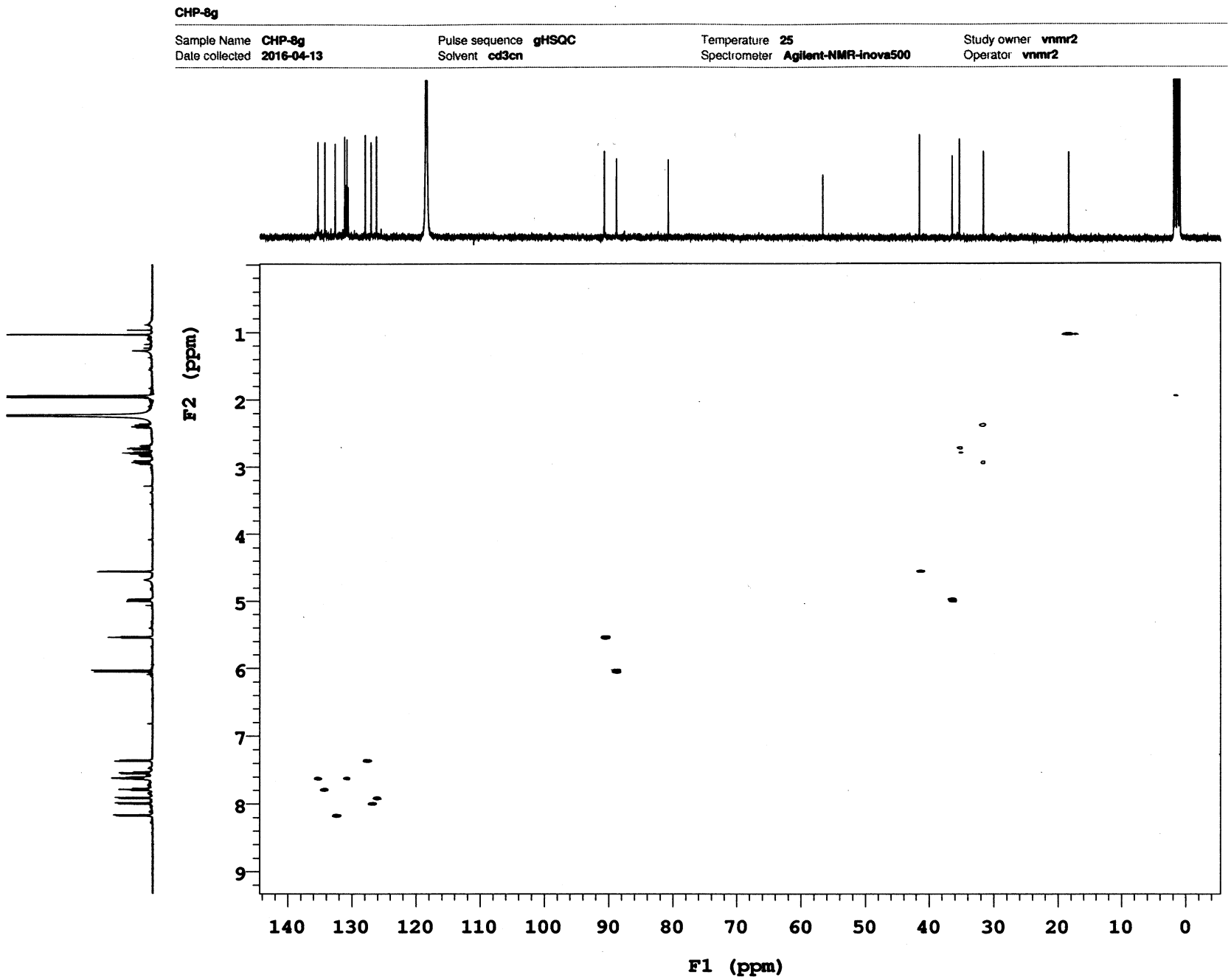
Fig S142. DEPT of compound 5i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g/DEPT_01

Plot date 2016-04-15

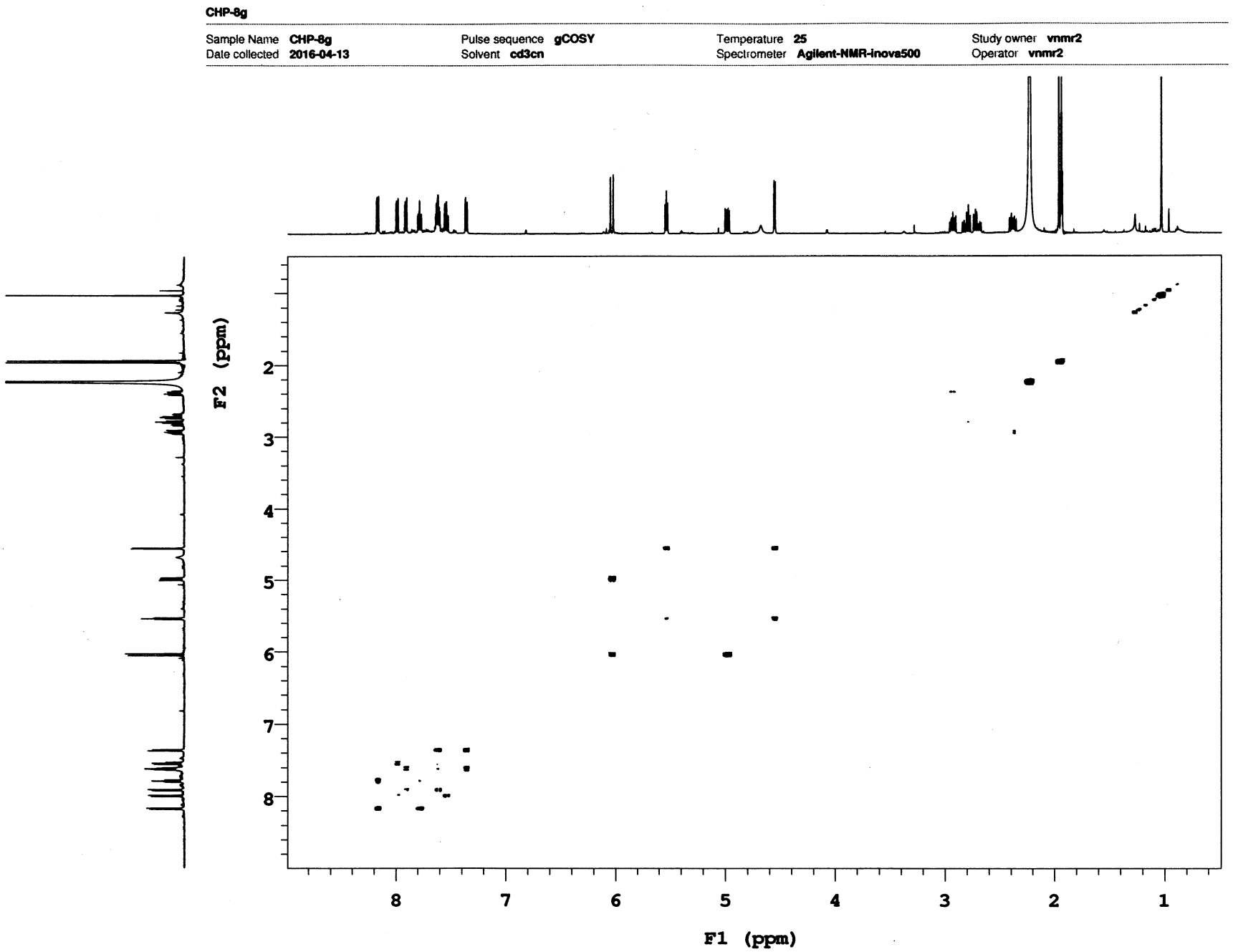
Fig S143. HSQC of compound 5i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g/gHSQC_01

Plot date 2016-04-15

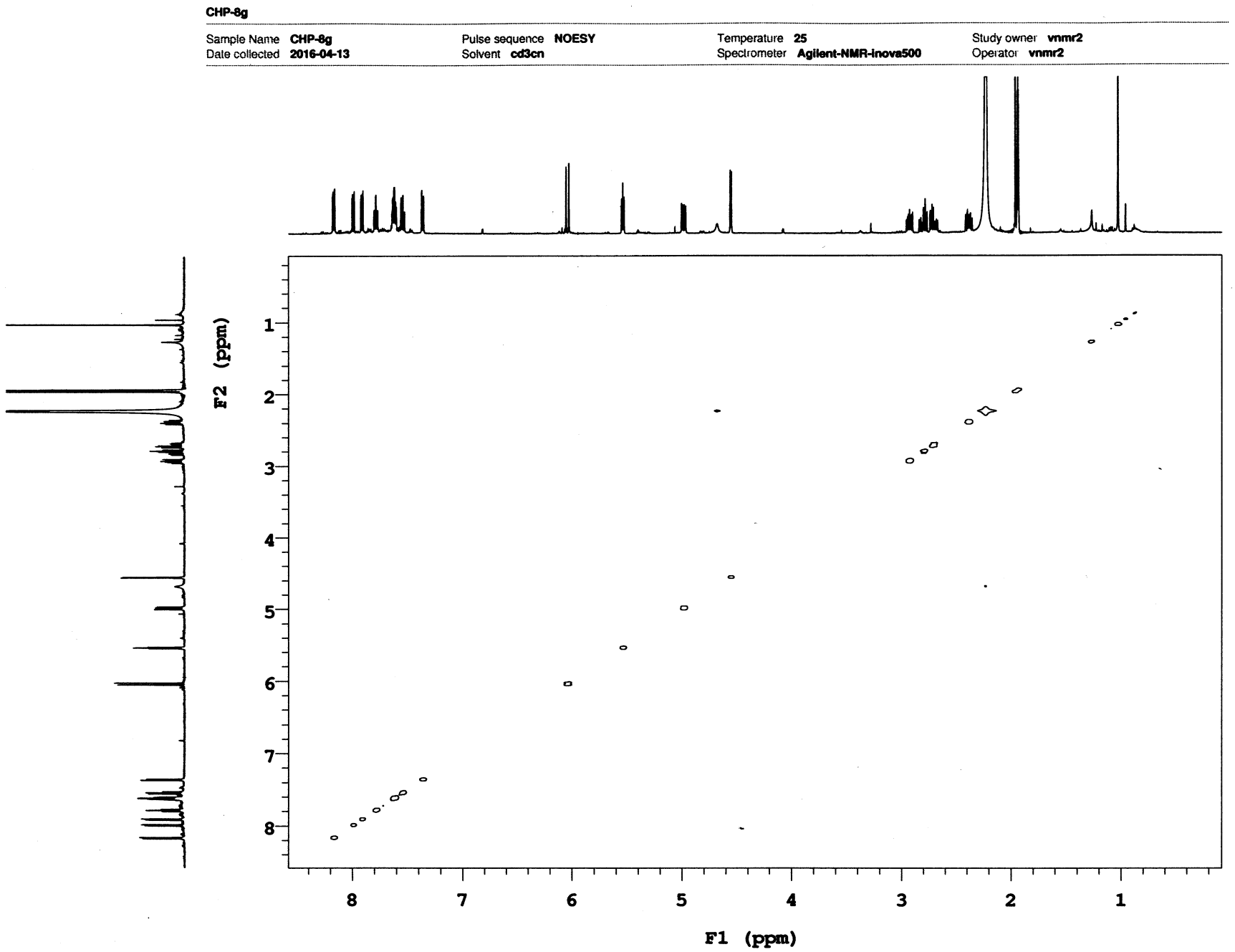
Fig S144. COSY of compound 5i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g/gCOSY_01

Plot date 2016-04-15

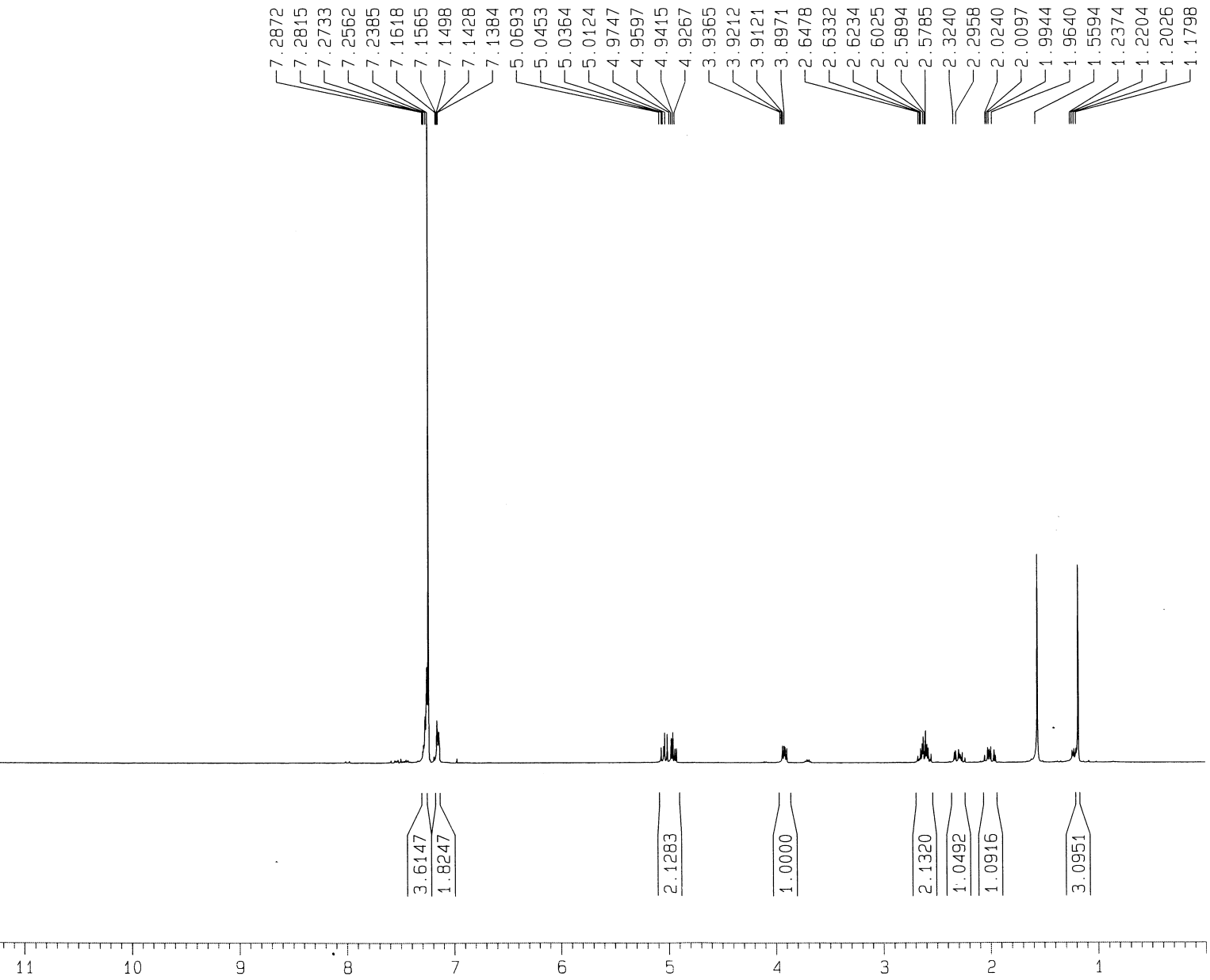
Fig S145. NOESY of compound 5i.



Data file /home/vnmr2/vnmrsys/data/511/CHP/CHP-8g/NOESY_01

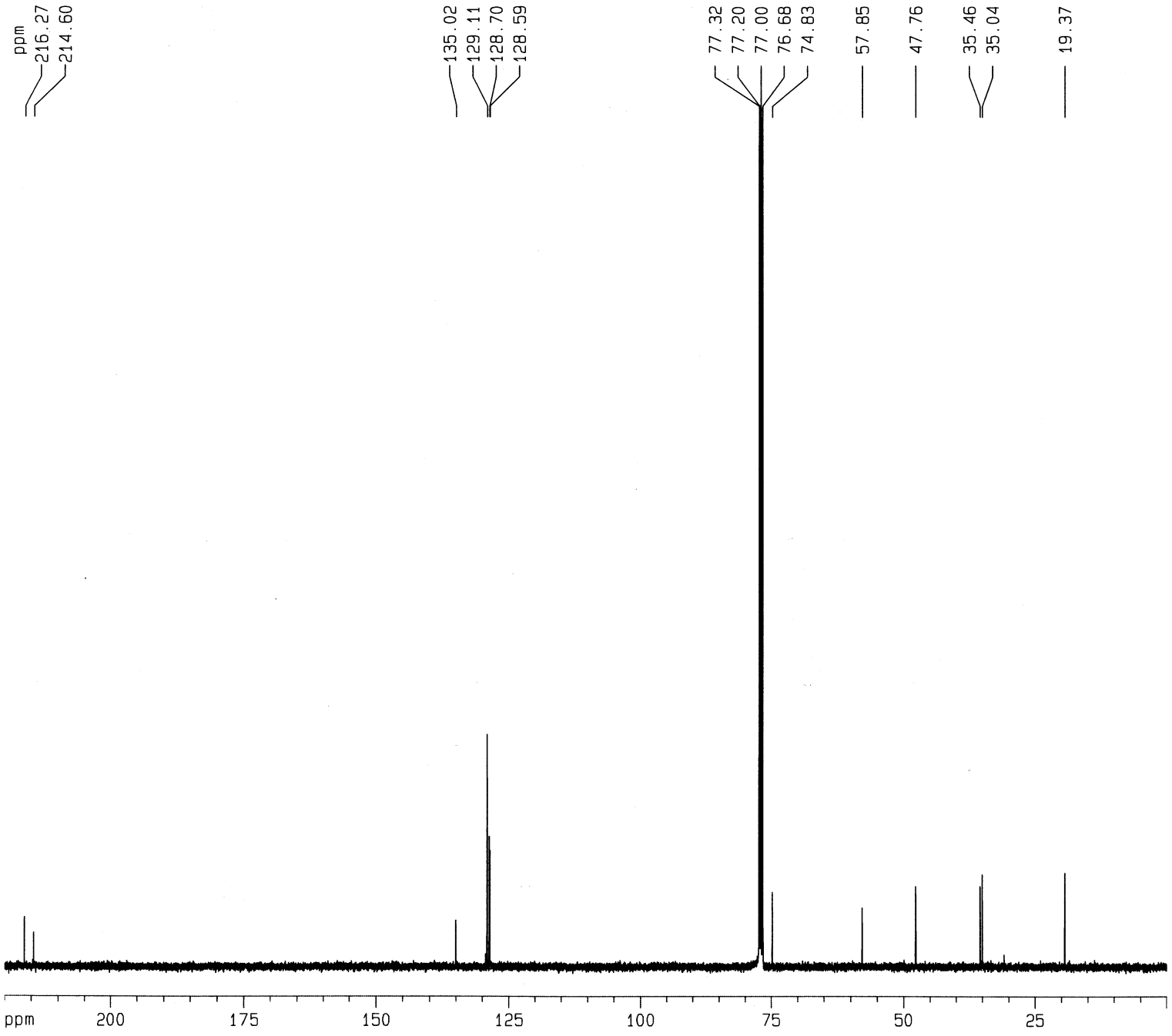
Plot date 2016-04-15

Fig S146. 1H NMR (CDCl3, 400 MHz) of compound 4a.



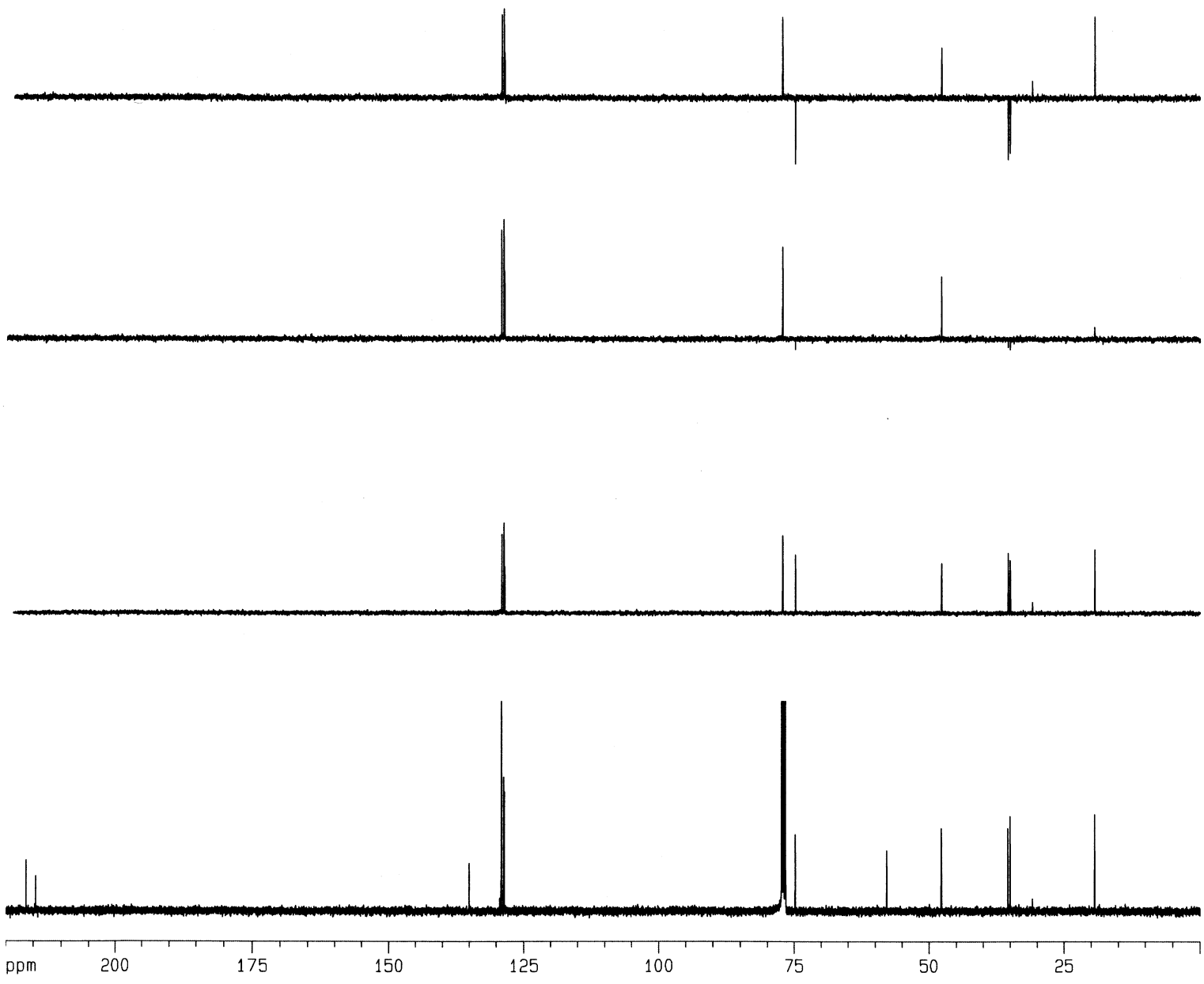

```
Current Data Parameters
NAME        CJW-2-20-top
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141113
Time               14.13
INSTRUM            spect
PROBHD     5 mm QNP  1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             5995.204 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                4597.6
DW                83.400 usec
DE                 6.50 usec
TE                300.0 K
D1             1.50000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                 11.90 usec
PL1                -3.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                  8192
SF          400.1300179 MHz
WDW                 EM
SSB                  0
LB                0.10 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX                21.50 cm
F1P              12.000 ppm
F1               4801.56 Hz
F2P              -0.000 ppm
F2               -0.00 Hz
PPMCM           0.55814 ppm/cm
HZCM          223.32838 Hz/cm
```

Fig S147. 13C NMR (CDCl3, 100 MHz) of compound 4a.




```
Current Data Parameters
NAME        CJW-2-20-top
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141114
Time                4.37
INSTRUM            spect
PROBHD     5 mm QNP  1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  5120
DS                     4
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                   256
DW                19.900 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                10.20 usec
PL1                0.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              14.50 dB
PL13              17.50 dB
SFO2         400.1326008 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127715 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                20.00 cm
F1P              220.000 ppm
F1             22134.81 Hz
F2P               0.000 ppm
F2                0.00 Hz
PPMCM          11.00000 ppm/cm
HZCM         1106.74048 Hz/cm
```

Fig S148. DEPT of compound 4a.



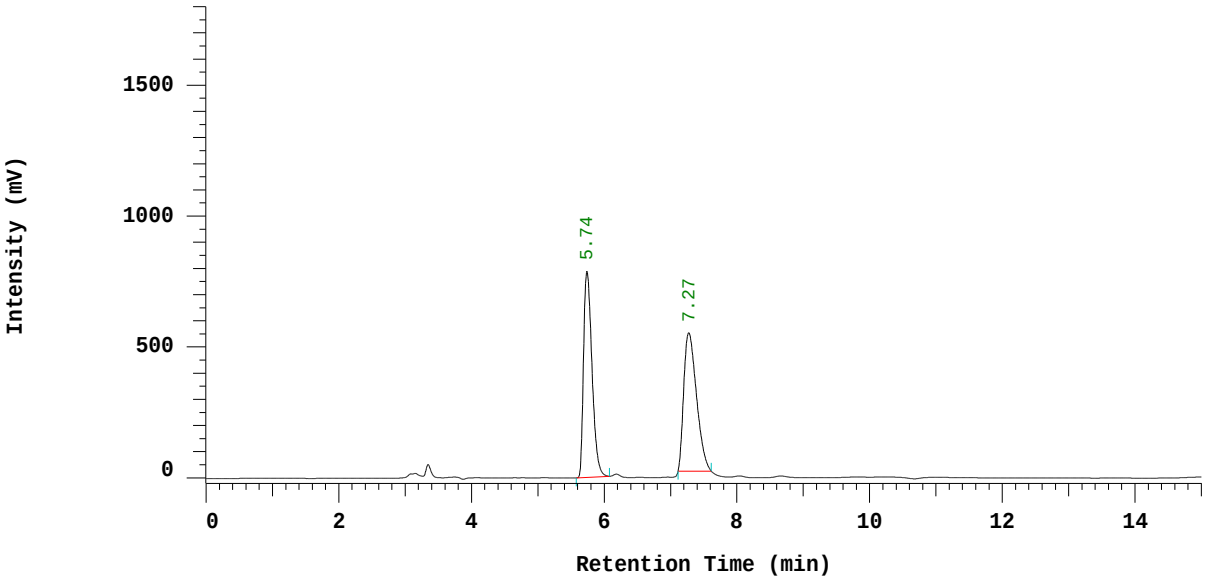

```
Current Data Parameters
NAME        CJW-2-20-top
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141114
Time                4.37
INSTRUM            spect
PROBHD     5 mm QNP  1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  5120
DS                     4
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                   256
DW                19.900 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                10.20 usec
PL1                0.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              14.50 dB
PL13              17.50 dB
SFO2         400.1326008 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127715 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                20.00 cm
F1P              220.000 ppm
F1             22134.81 Hz
F2P              0.000 ppm
F2               0.00 Hz
PPMCM          11.00000 ppm/cm
HZCM         1106.74048 Hz/cm
```

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 03/04/2016 01:33 PM
Reported Date and Time: 03/06/2016 02:14 PM
Processed Date and Time: 03/06/2016 02:13 PM
Data Path: D:\Arun\DATA\0427\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0427
Application(data): Arun
Vial Number: 1
Sample Name: CHP-01-50
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 13%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 217 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 217 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.74	6951809	787157	49.727
2	7.27	7028108	528549	50.273
		13979917	1315706	100.000

Peak rejection level: 5000

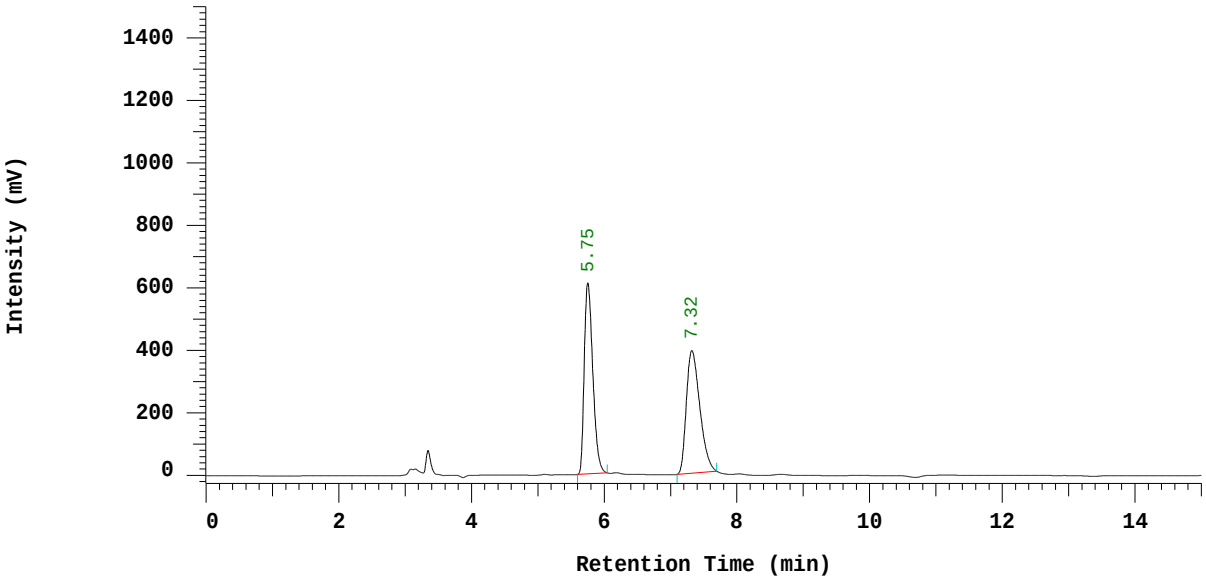
Fig S149. HPLC analysis of the compound **3a** obtained, (Table 1, entry 6)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 03/04/2016 01:58 PM
Reported Date and Time: 03/06/2016 02:09 PM
Processed Date and Time: 03/06/2016 02:08 PM
Data Path: D:\Arun\DATA\0428\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0428
Application(data): Arun
Vial Number: 1
Sample Name: CHP-01-51
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 13%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 217 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 217 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.75	5453257	611259	49.736
2	7.32	5511103	392354	50.264
		10964360	1003613	100.000

Peak rejection level: 5000

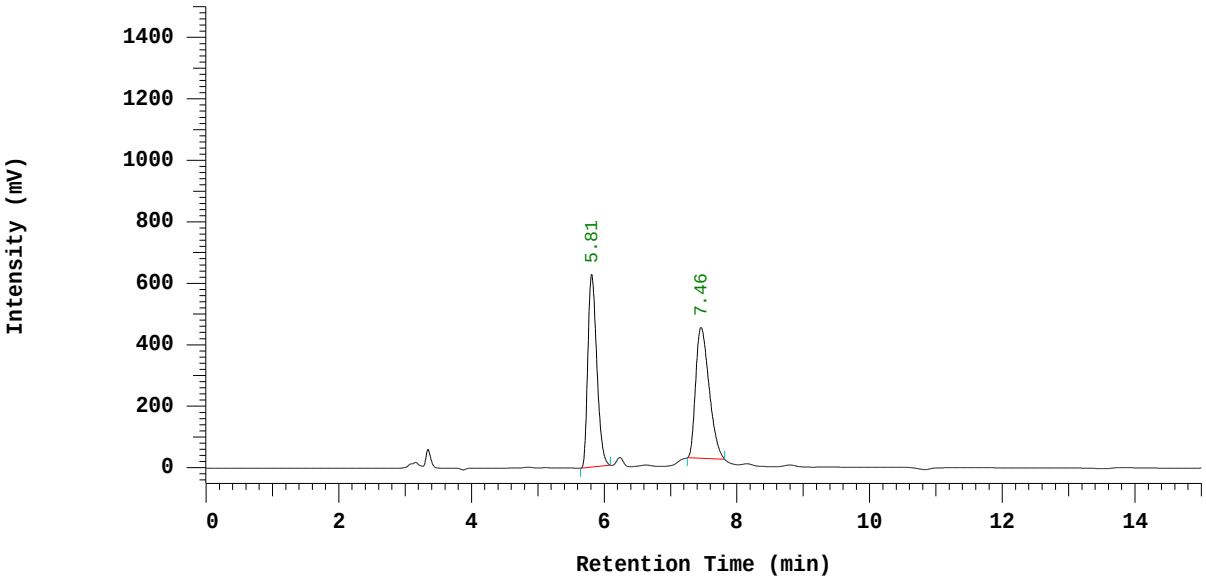
Fig S150. HPLC analysis of the compound **3a** obtained, (Table 1, entry 7)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 03/04/2016 02:57 PM
Reported Date and Time: 03/06/2016 02:06 PM
Processed Date and Time: 03/06/2016 02:06 PM
Data Path: D:\Arun\DATA\0429\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0429
Application(data): Arun
Vial Number: 1
Sample Name: CHP-01-52
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 13%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 217 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 217 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.81	5885371	626405	49.589
2	7.46	5983016	425624	50.411
		11868387	1052029	100.000

Peak rejection level: 5000

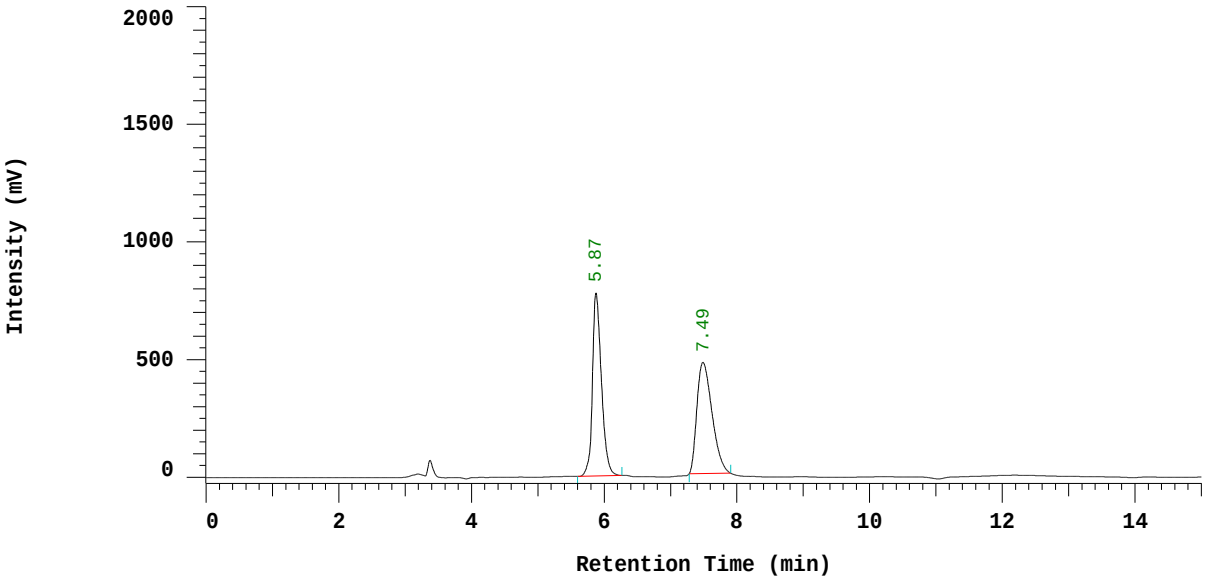
Fig S151. HPLC analysis of the compound **3a** obtained, (Table 1, entry 8)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 03/03/2016 04:10 PM
Reported Date and Time: 03/03/2016 04:40 PM
Processed Date and Time: 03/03/2016 04:39 PM
Data Path: D:\Arun\DATA\0426\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0426
Application(data): Arun
Vial Number: 1
Sample Name: AR-03-173 (Racemic)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 13%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 217 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 217 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.87	7350442	777507	49.556
2	7.49	7482187	472766	50.444
		14832629	1250273	100.000

Peak rejection level: 5000

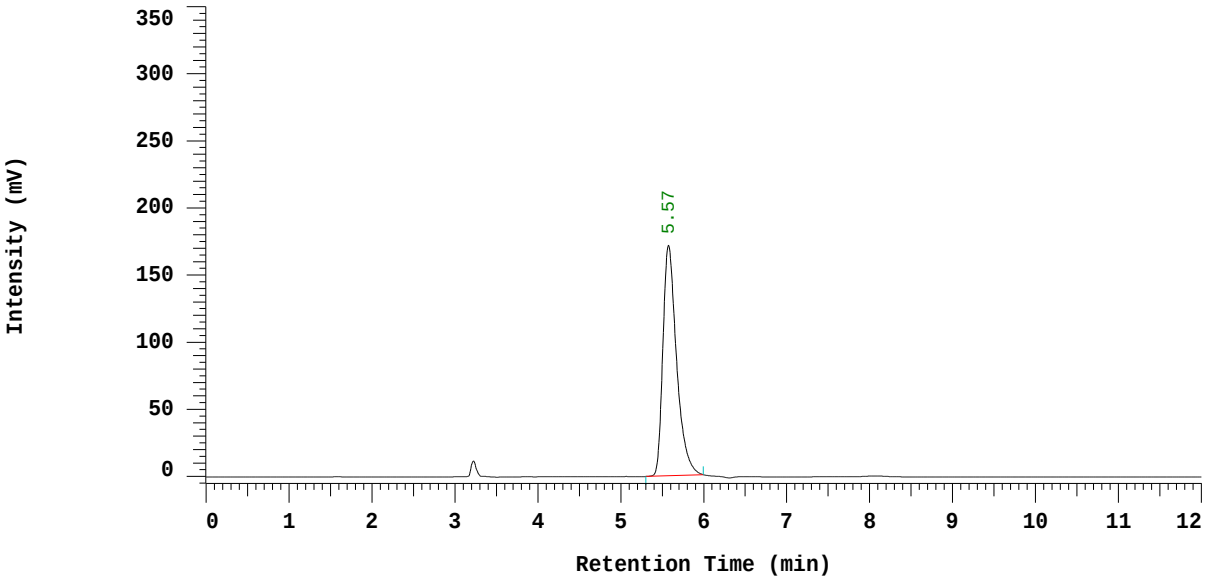
Fig S152. HPLC analysis of the compound **3a** obtained, (Table 1, entry 9)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/23/2016 05:55 PM
Reported Date and Time: 07/01/2016 01:13 PM
Processed Date and Time: 07/01/2016 01:13 PM
Data Path: D:\Arun\DATA\0469\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0469
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crystal 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.57	1965962	171710	100.000
		1965962	171710	100.000

Peak rejection level: 5000

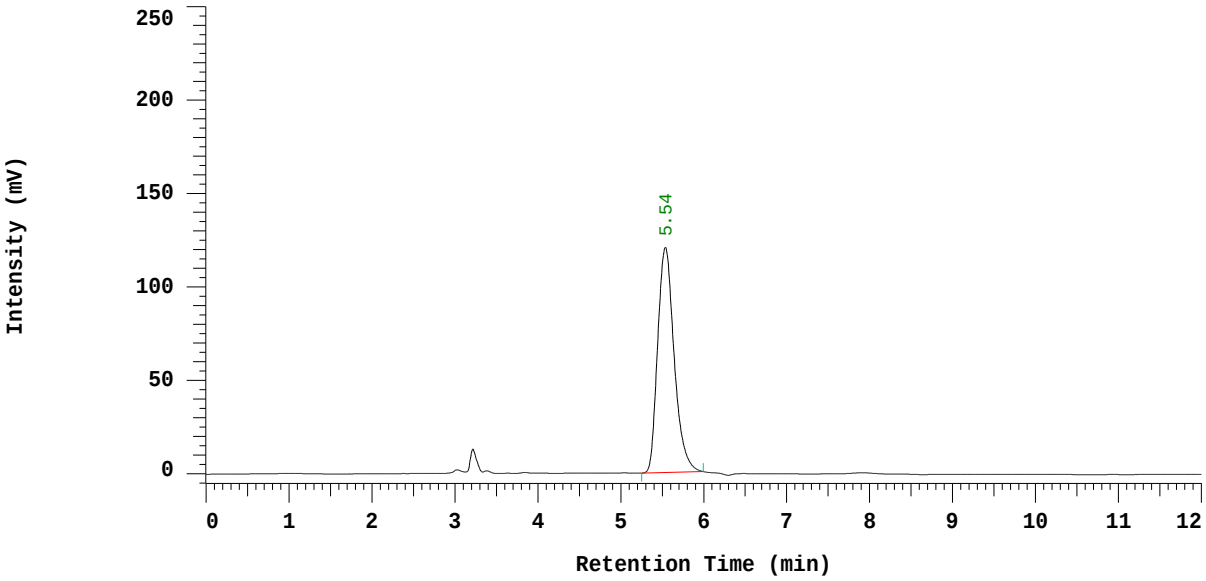
Fig S153. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 1)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/24/2016 12:22 PM
Reported Date and Time: 07/01/2016 01:07 PM
Processed Date and Time: 07/01/2016 01:07 PM
Data Path: D:\Arun\DATA\0474\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0474
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.54	1660111	120449	100.000
		1660111	120449	100.000

Peak rejection level: 5000

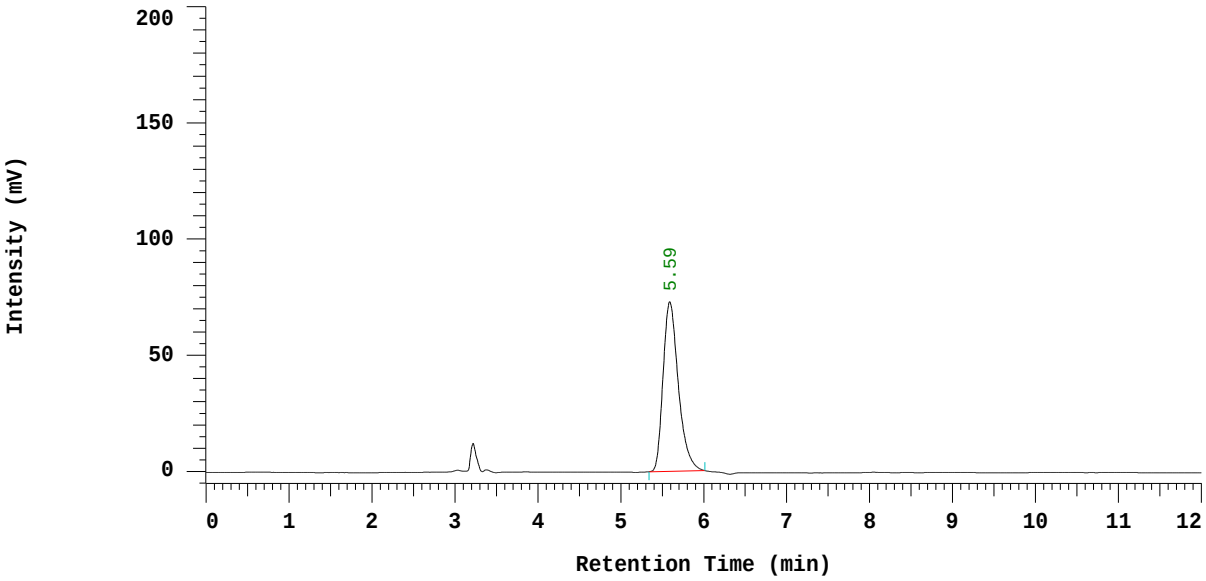
Fig S154. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 2)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/24/2016 12:50 PM
Reported Date and Time: 07/01/2016 01:04 PM
Processed Date and Time: 07/01/2016 01:04 PM
Data Path: D:\Arun\DATA\0476\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0476
Application(data): Arun
Vial Number: 3
Sample Name: CHP-8g-F2 (Crys 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.59	932401	72897	100.000
		932401	72897	100.000

Peak rejection level: 5000

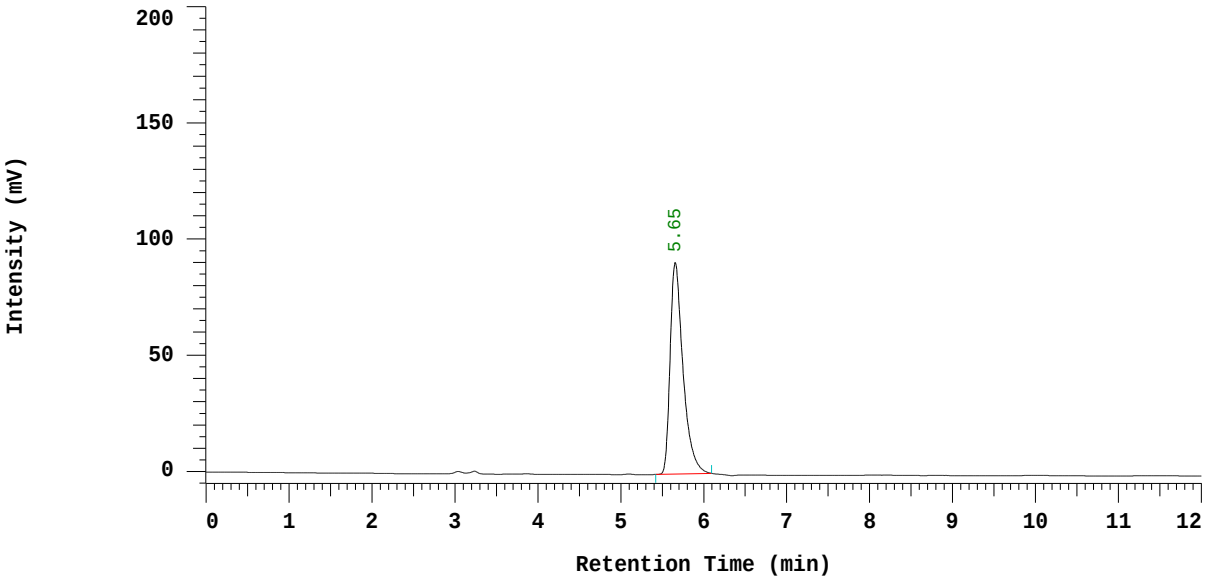
Fig S155. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 3)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/26/2016 04:01 PM
Reported Date and Time: 07/01/2016 12:55 PM
Processed Date and Time: 07/01/2016 12:54 PM
Data Path: D:\Arun\DATA\0480\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0480
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.65	982521	90981	100.000
		982521	90981	100.000

Peak rejection level: 5000

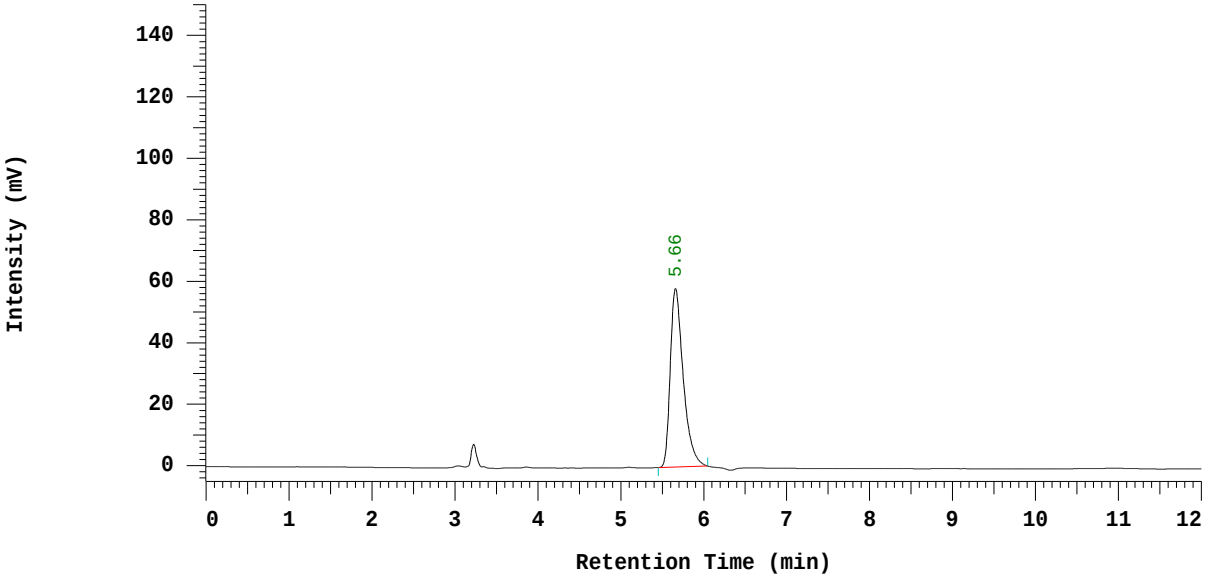
Fig S156. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 4)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/26/2016 04:15 PM
Reported Date and Time: 07/01/2016 12:53 PM
Processed Date and Time: 07/01/2016 12:53 PM
Data Path: D:\Arun\DATA\0481\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0481
Application(data): Arun
Vial Number: 2
Sample Name: CHP-8g-F2 (Crys 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.66	629116	58061	100.000
		629116	58061	100.000

Peak rejection level: 5000

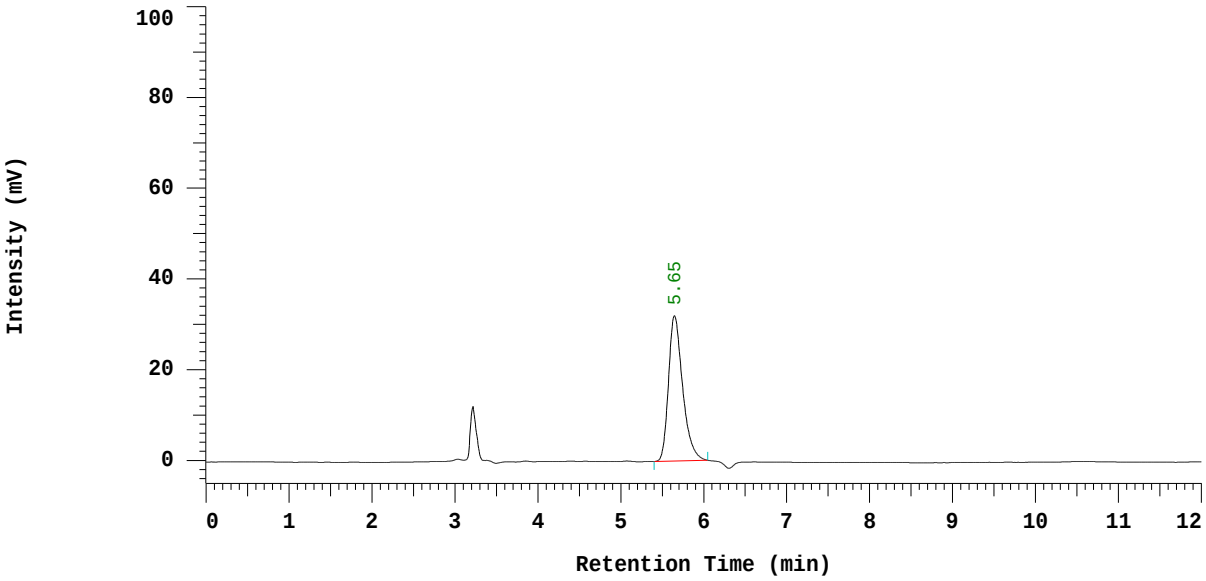
Fig S157. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 5)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/26/2016 04:28 PM
Reported Date and Time: 07/01/2016 12:52 PM
Processed Date and Time: 07/01/2016 12:51 PM
Data Path: D:\Arun\DATA\0482\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0482
Application(data): Arun
Vial Number: 3
Sample Name: CHP-8g-F2 (Crys 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.65	378230	32017	100.000
		378230	32017	100.000

Peak rejection level: 5000

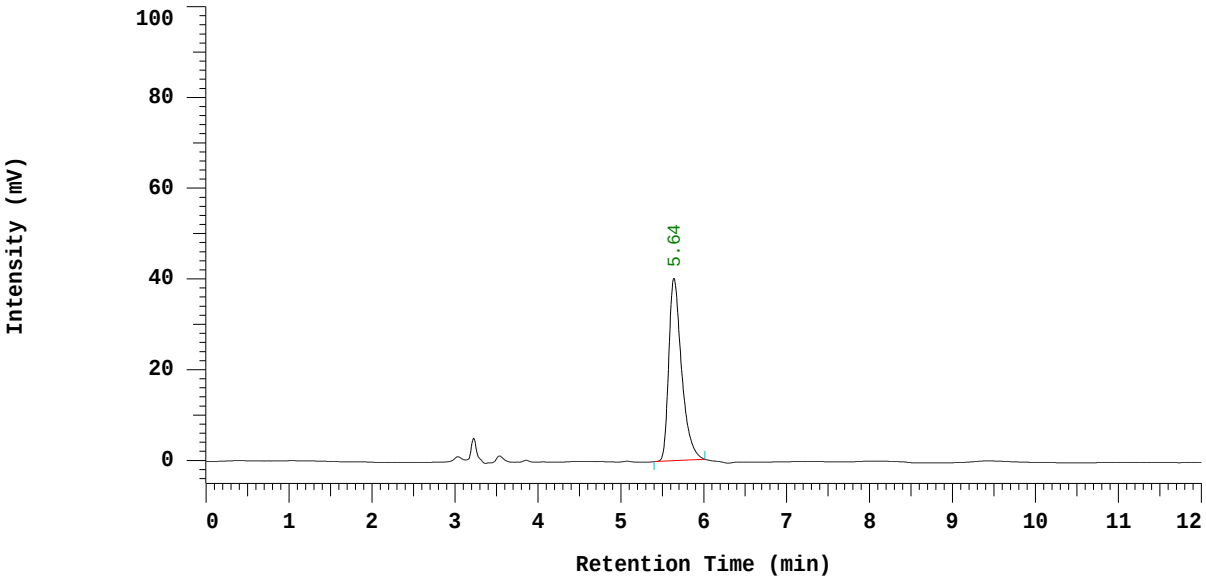
Fig S158. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 6)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 04:18 PM
Reported Date and Time: 07/01/2016 12:44 PM
Processed Date and Time: 07/01/2016 12:44 PM
Data Path: D:\Arun\DATA\0486\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0486
Application(data): Arun
Vial Number: 2
Sample Name: CHP-8g-F2 (Crys 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.64	431230	40210	100.000
		431230	40210	100.000

Peak rejection level: 5000

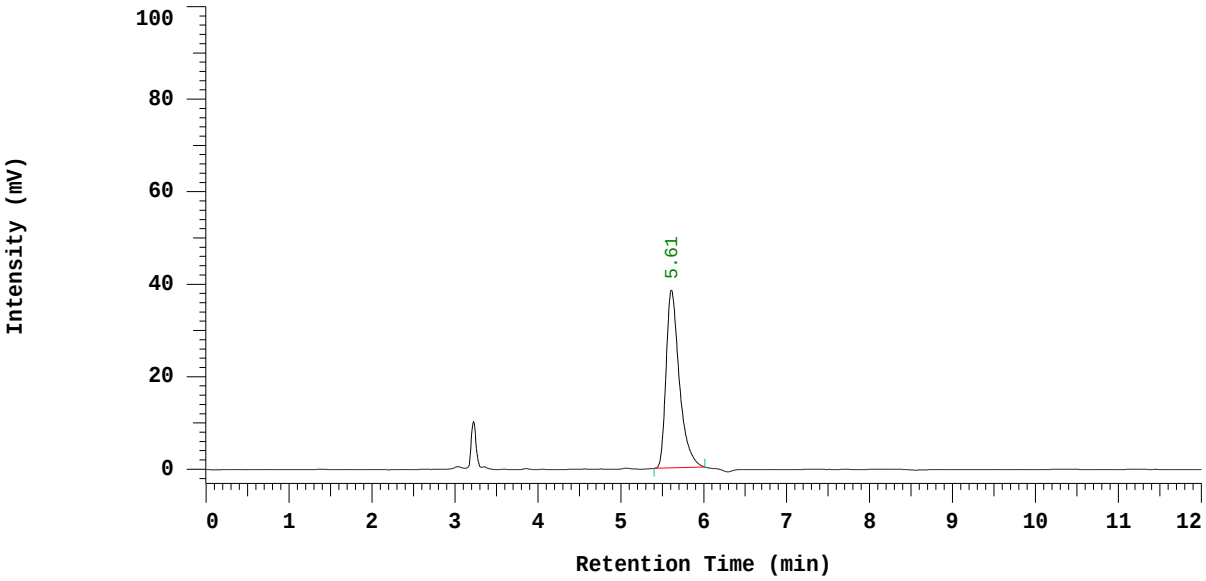
Fig S159. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 7)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 06:00 PM
Reported Date and Time: 07/01/2016 12:32 PM
Processed Date and Time: 07/01/2016 12:32 PM
Data Path: D:\Arun\DATA\0493\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0493
Application(data): Arun
Vial Number: 4
Sample Name: CHP-8g-F2 (Crys 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.61	426716	38449	100.000
		426716	38449	100.000

Peak rejection level: 5000

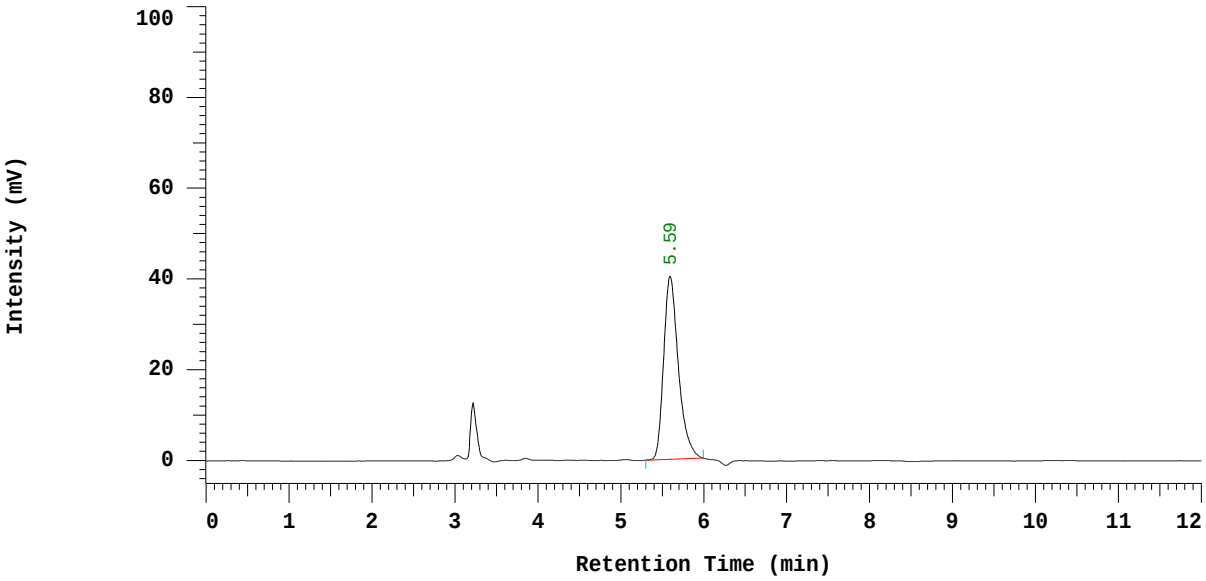
Fig S160. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 8)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 06:16 PM
Reported Date and Time: 07/01/2016 12:30 PM
Processed Date and Time: 07/01/2016 12:29 PM
Data Path: D:\Arun\DATA\0494\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0494
Application(data): Arun
Vial Number: 5
Sample Name: CHP-8g-F2 (Crys 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.59	498296	40384	100.000
		498296	40384	100.000

Peak rejection level: 5000

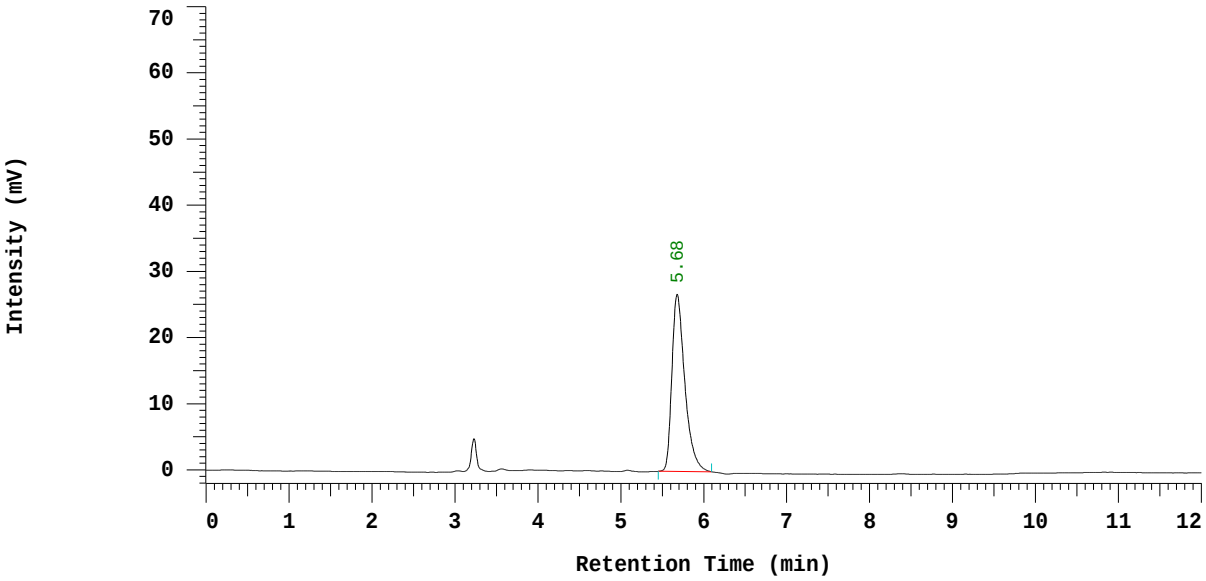
Fig S161. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 9)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 04:27 PM
Reported Date and Time: 07/01/2016 12:23 PM
Processed Date and Time: 07/01/2016 12:23 PM
Data Path: D:\Arun\DATA\0499\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0499
Application(data): Arun
Vial Number: 3
Sample Name: CHP-8g-F2 (Crys 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.68	289629	26775	100.000
		289629	26775	100.000

Peak rejection level: 5000

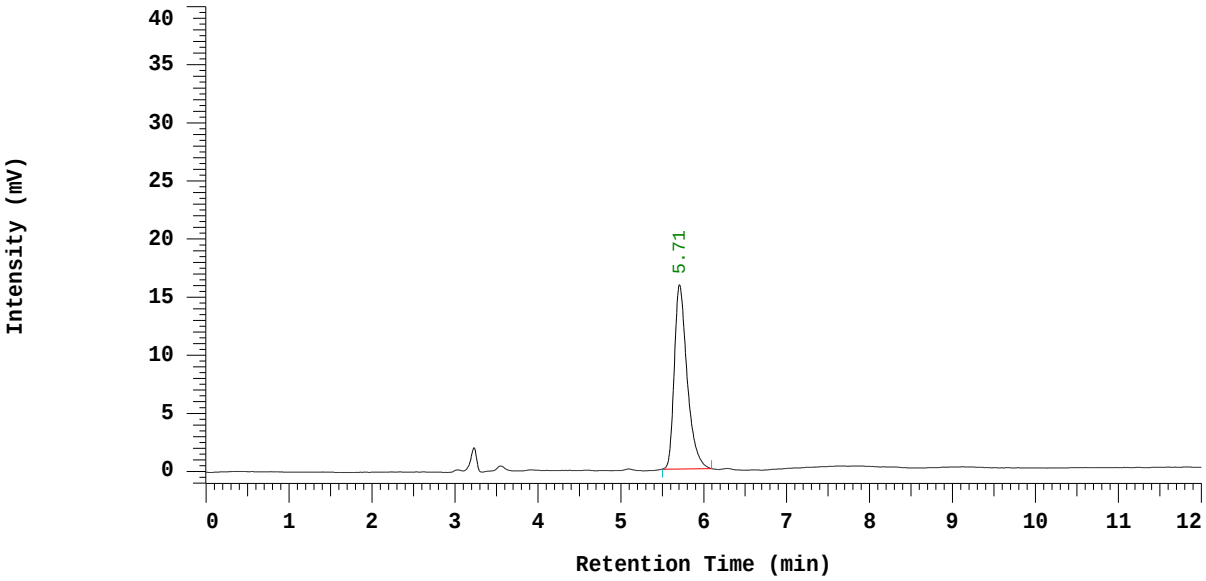
Fig S162. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 10)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 04:40 PM
Reported Date and Time: 07/01/2016 12:22 PM
Processed Date and Time: 07/01/2016 12:22 PM
Data Path: D:\Arun\DATA\0500\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0500
Application(data): Arun
Vial Number: 4
Sample Name: CHP-8g-F2 (Crys 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.71	170488	15853	100.000
		170488	15853	100.000

Peak rejection level: 5000

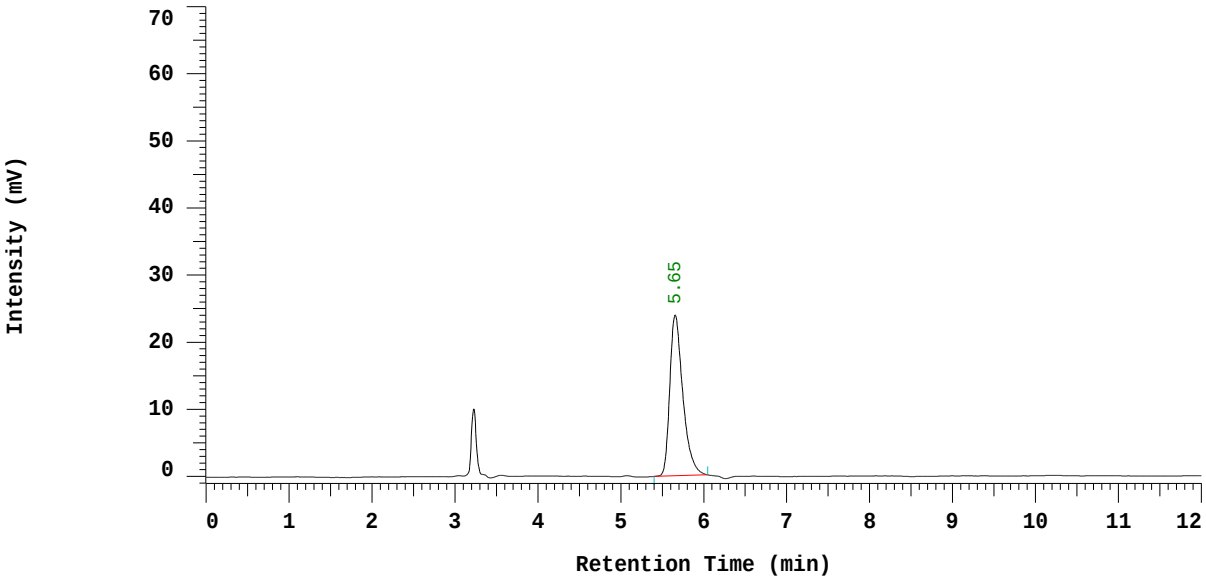
Fig S163. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 11)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 05:34 PM
Reported Date and Time: 07/01/2016 12:15 PM
Processed Date and Time: 07/01/2016 12:14 PM
Data Path: D:\Arun\DATA\0504\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0504
Application(data): Arun
Vial Number: 3
Sample Name: CHP-8g-F2 (Crys 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.65	261816	23954	100.000
		261816	23954	100.000

Peak rejection level: 5000

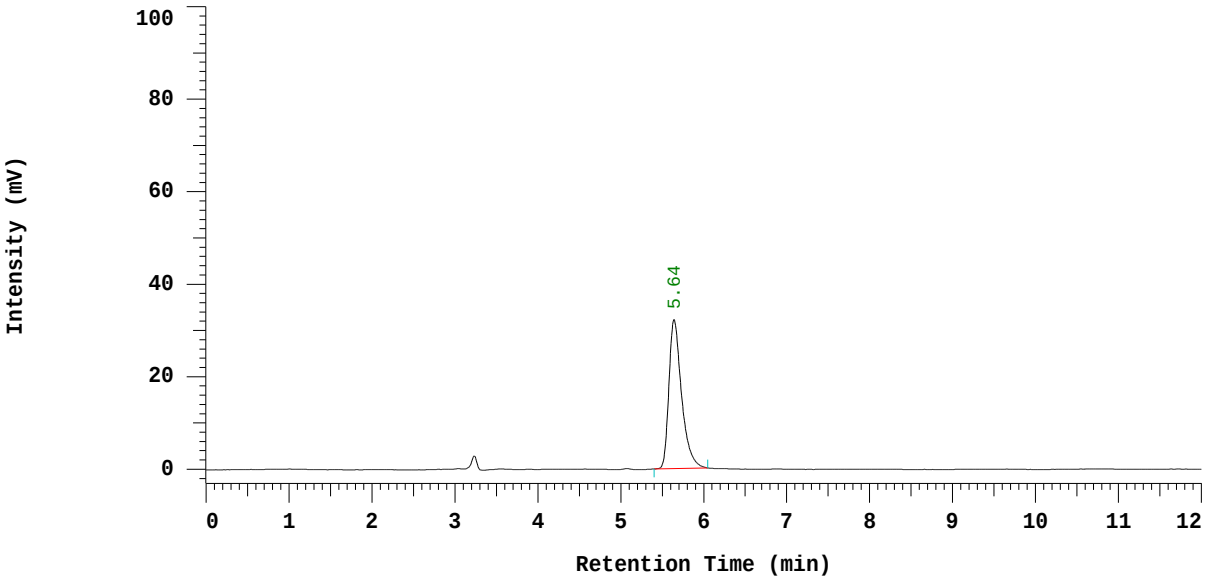
Fig S164. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 12)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 05:47 PM
Reported Date and Time: 07/01/2016 12:13 PM
Processed Date and Time: 07/01/2016 12:12 PM
Data Path: D:\Arun\DATA\0505\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0505
Application(data): Arun
Vial Number: 4
Sample Name: CHP-8g-F2 (Crys 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.64	341129	32185	100.000
		341129	32185	100.000

Peak rejection level: 5000

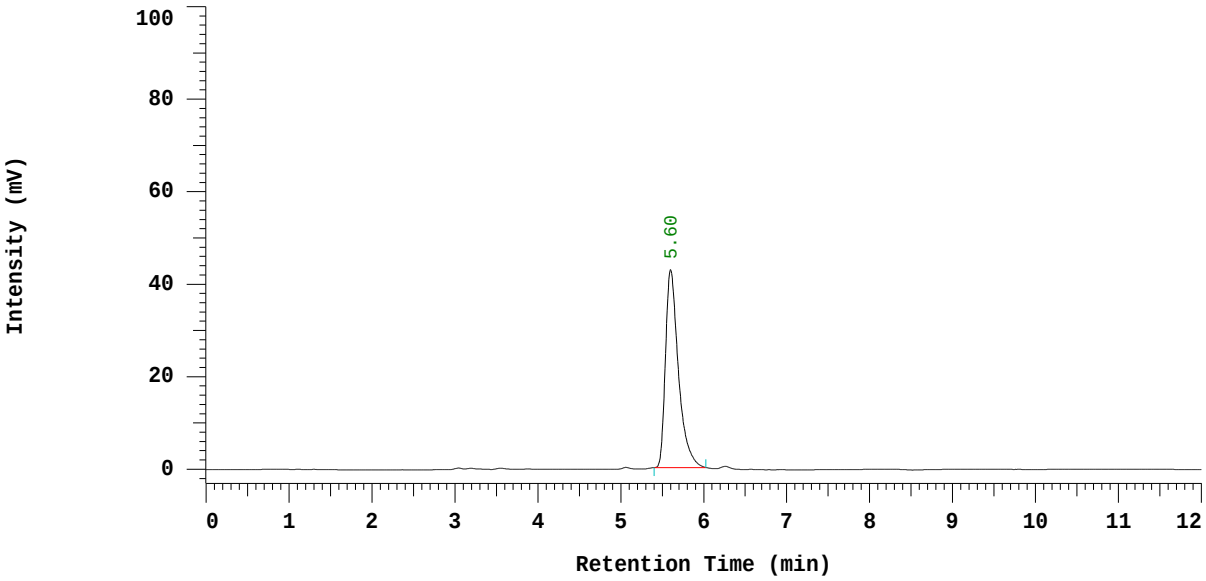
Fig S165. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 13)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 04:59 PM
Reported Date and Time: 07/01/2016 11:58 AM
Processed Date and Time: 07/01/2016 11:57 AM
Data Path: D:\Arun\DATA\0515\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0515
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.60	463194	42825	100.000
		463194	42825	100.000

Peak rejection level: 5000

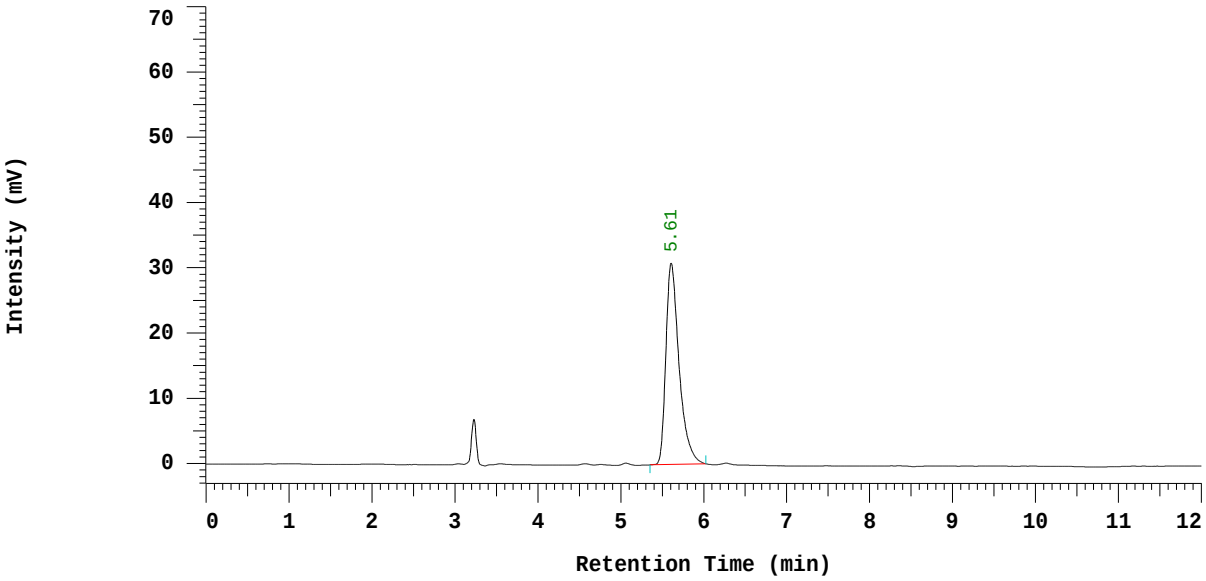
Fig S166. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 14)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 05:12 PM
Reported Date and Time: 07/01/2016 11:56 AM
Processed Date and Time: 07/01/2016 11:55 AM
Data Path: D:\Arun\DATA\0516\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0516
Application(data): Arun
Vial Number: 2
Sample Name: CHP-8g-F2 (Crys 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.61	340930	30841	100.000
		340930	30841	100.000

Peak rejection level: 5000

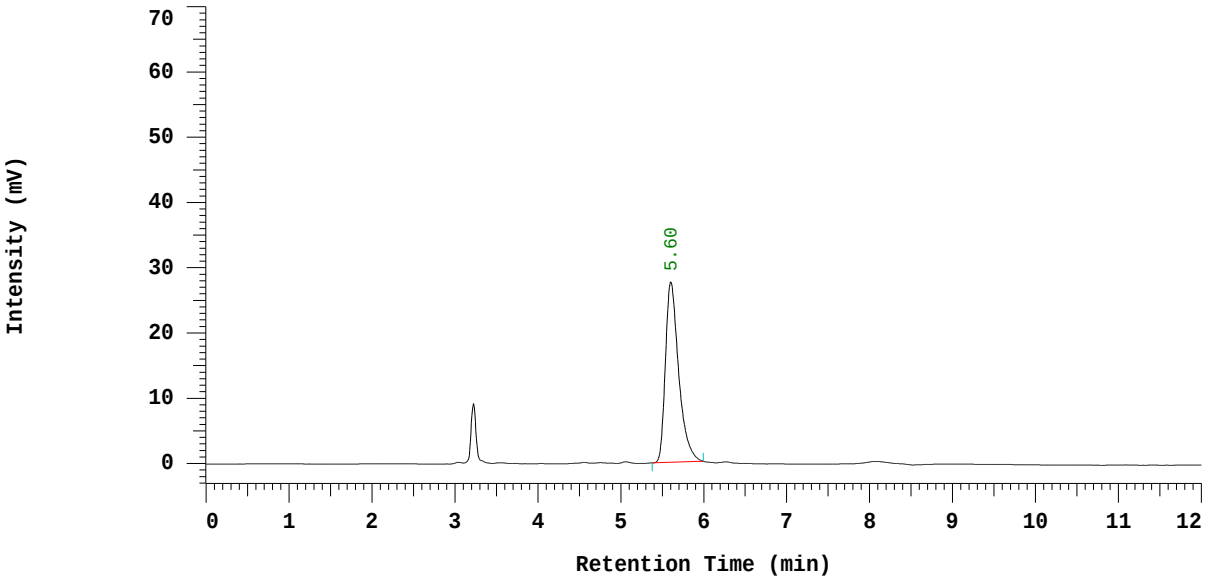
Fig S167. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 15)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 05:50 PM
Reported Date and Time: 07/01/2016 11:49 AM
Processed Date and Time: 07/01/2016 11:49 AM
Data Path: D:\Arun\DATA\0519\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0519
Application(data): Arun
Vial Number: 5
Sample Name: CHP-8g-F2 (Crys 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.60	306252	27617	100.000
		306252	27617	100.000

Peak rejection level: 5000

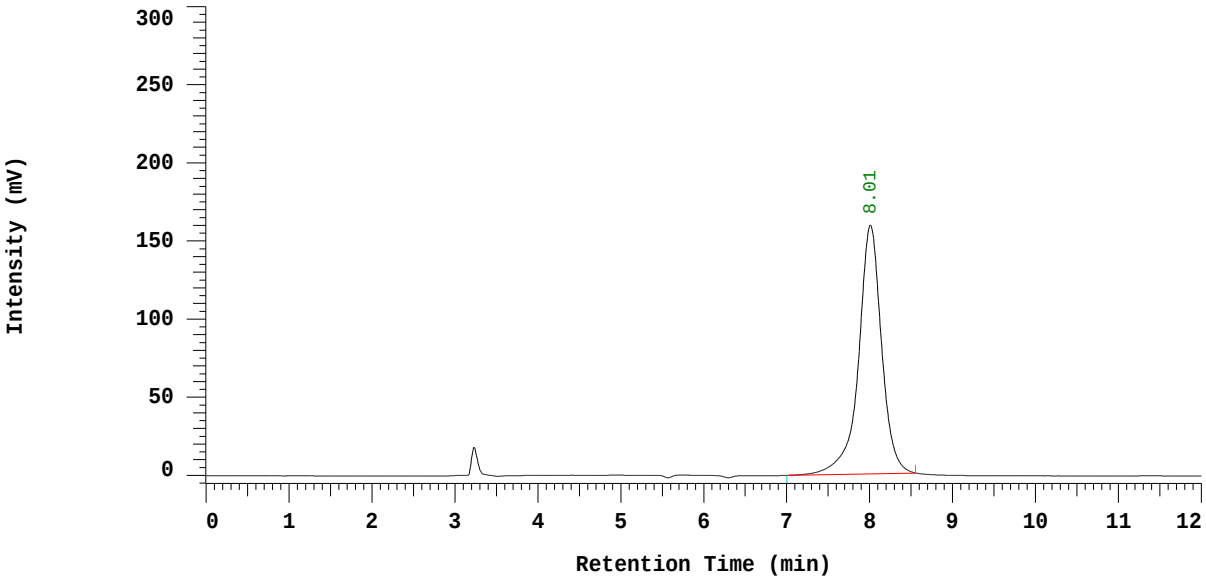
Fig S168. HPLC analysis of a crystal of the (+)-**3i** obtained (crystal count number 16)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/23/2016 05:39 PM
Reported Date and Time: 07/01/2016 01:14 PM
Processed Date and Time: 07/01/2016 01:14 PM
Data Path: D:\Arun\DATA\0468\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0468
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crystal 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.01	3072195	159115	100.000
		3072195	159115	100.000

Peak rejection level: 5000

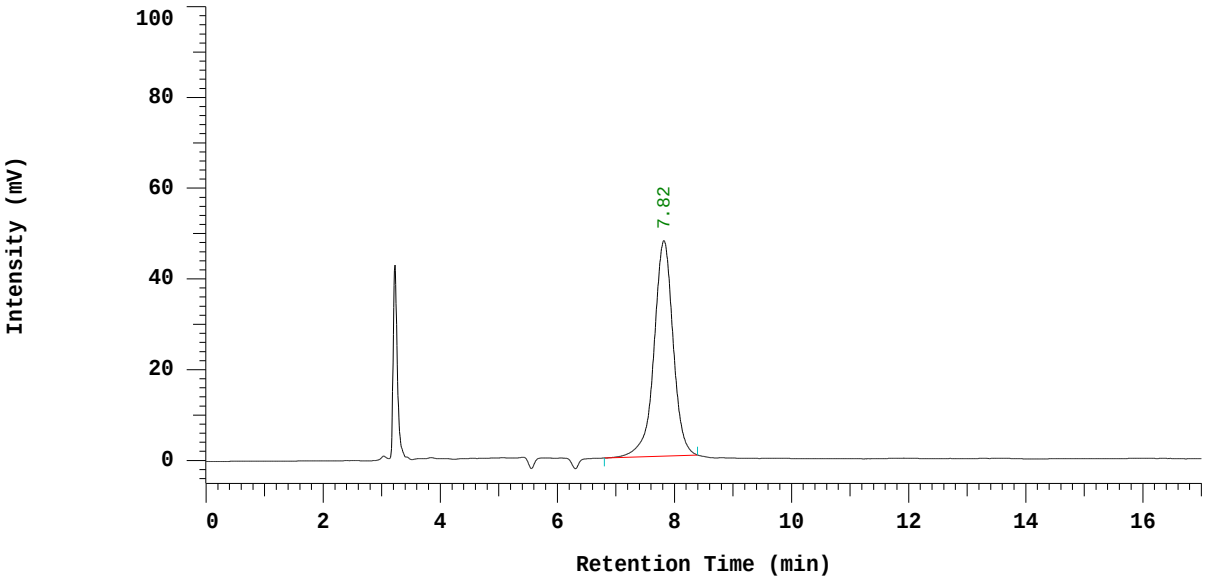
Fig S169. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 1)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/23/2016 09:15 PM
Reported Date and Time: 07/01/2016 01:09 PM
Processed Date and Time: 07/01/2016 01:09 PM
Data Path: D:\Arun\DATA\0472\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0472
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crystal 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	7.82	1075182	47439	100.000
		1075182	47439	100.000

Peak rejection level: 5000

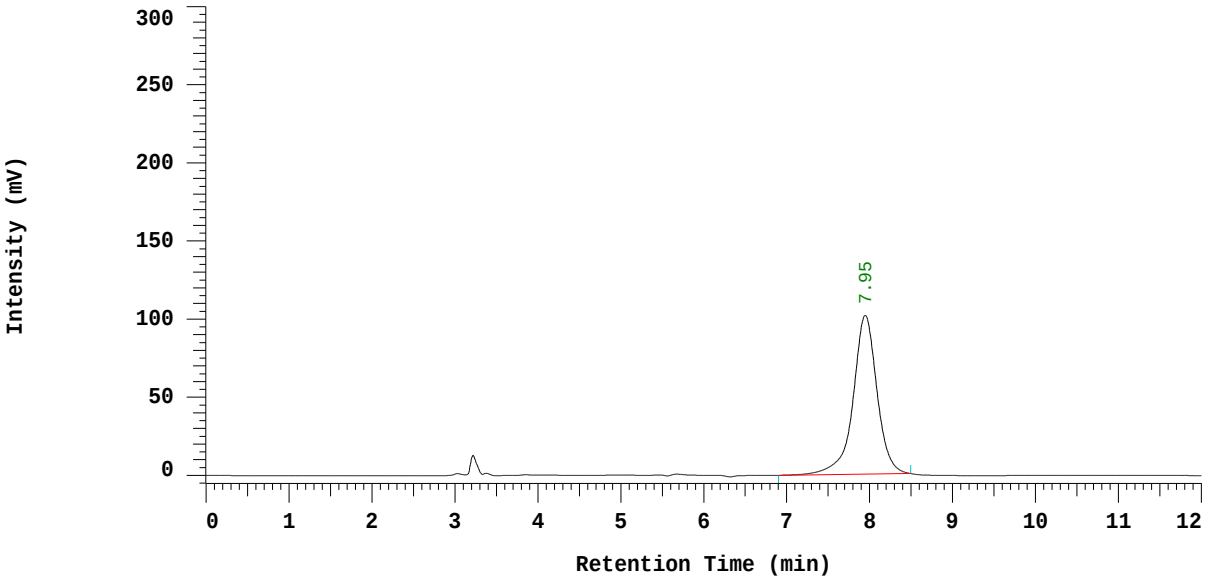
Fig S170. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 2)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/24/2016 12:35 PM
Reported Date and Time: 07/01/2016 01:06 PM
Processed Date and Time: 07/01/2016 01:06 PM
Data Path: D:\Arun\DATA\0475\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0475
Application(data): Arun
Vial Number: 2
Sample Name: CHP-8g-F2 (Crys 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	7.95	2042287	101574	100.000
		2042287	101574	100.000

Peak rejection level: 5000

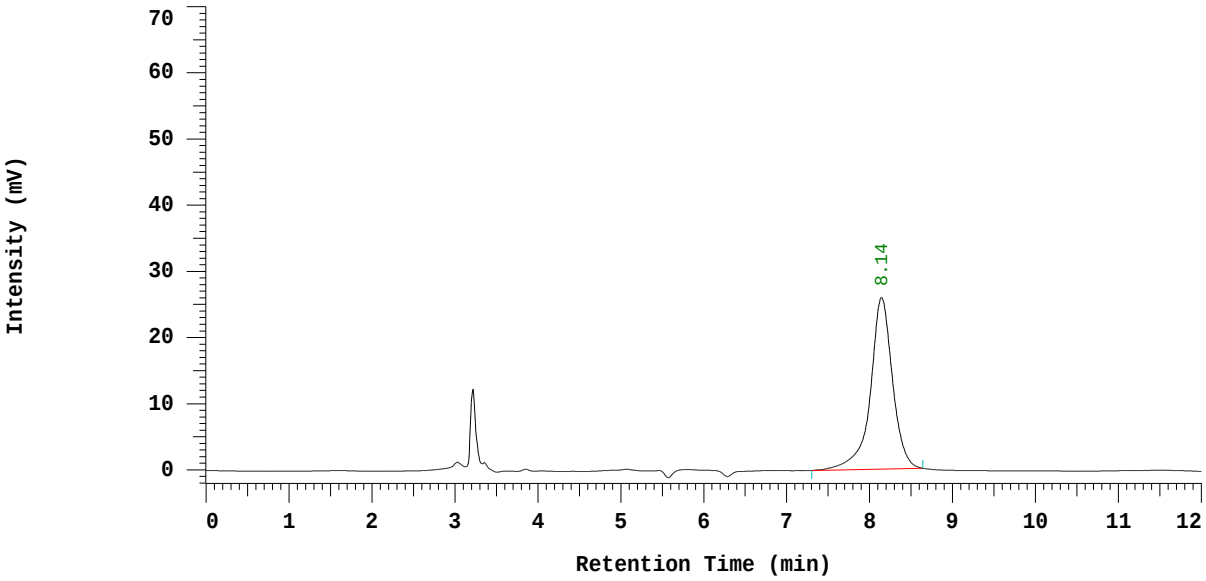
Fig S171. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 3)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 04:31 PM
Reported Date and Time: 07/01/2016 12:43 PM
Processed Date and Time: 07/01/2016 12:42 PM
Data Path: D:\Arun\DATA\0487\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0487
Application(data): Arun
Vial Number: 3
Sample Name: CHP-8g-F2 (Crys 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.14	481174	25906	100.000
		481174	25906	100.000

Peak rejection level: 5000

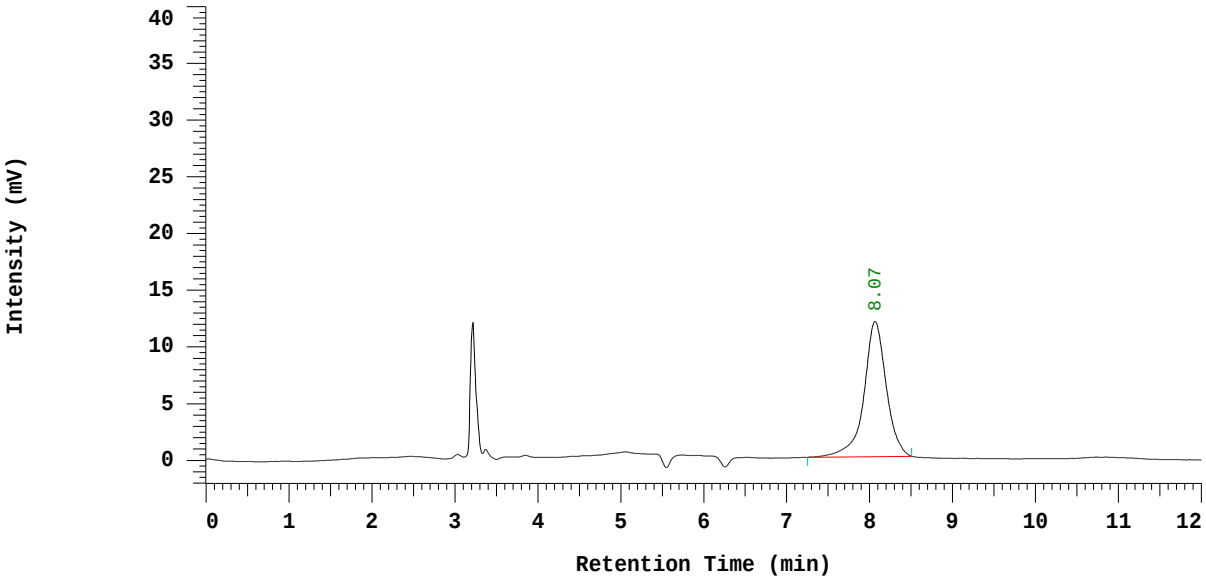
Fig S172. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 4)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 04:44 PM
Reported Date and Time: 07/01/2016 12:41 PM
Processed Date and Time: 07/01/2016 12:41 PM
Data Path: D:\Arun\DATA\0488\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0488
Application(data): Arun
Vial Number: 4
Sample Name: CHP-8g-F2 (Crys 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.07	222480	11916	100.000
		222480	11916	100.000

Peak rejection level: 5000

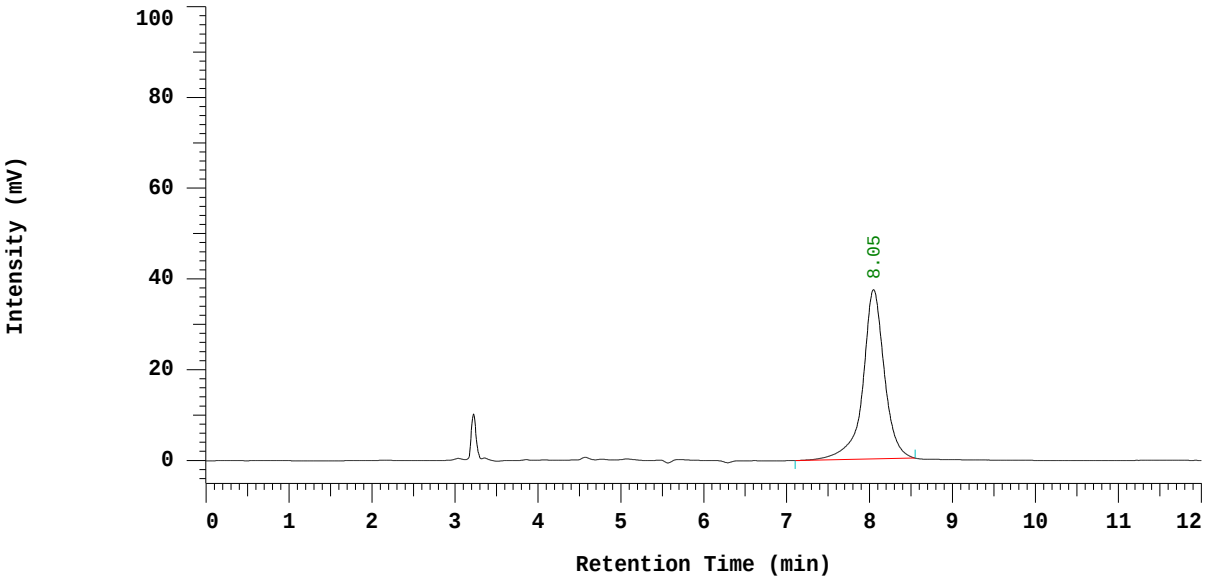
Fig S173. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 5)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 05:35 PM
Reported Date and Time: 07/01/2016 12:35 PM
Processed Date and Time: 07/01/2016 12:35 PM
Data Path: D:\Arun\DATA\0491\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0491
Application(data): Arun
Vial Number: 2
Sample Name: CHP-8g-F2 (Crys 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.05	672817	37319	100.000
		672817	37319	100.000

Peak rejection level: 5000

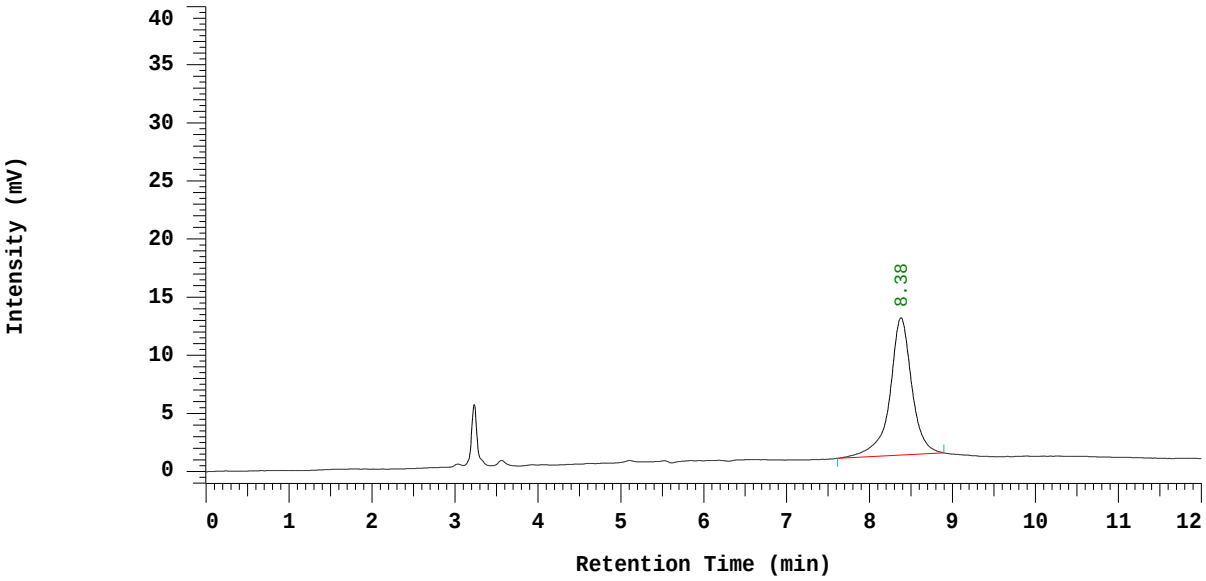
Fig S174. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 6)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 04:14 PM
Reported Date and Time: 07/01/2016 12:25 PM
Processed Date and Time: 07/01/2016 12:25 PM
Data Path: D:\Arun\DATA\0498\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0498
Application(data): Arun
Vial Number: 2
Sample Name: CHP-8g-F2 (Crys 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.38	217094	11818	100.000
		217094	11818	100.000

Peak rejection level: 5000

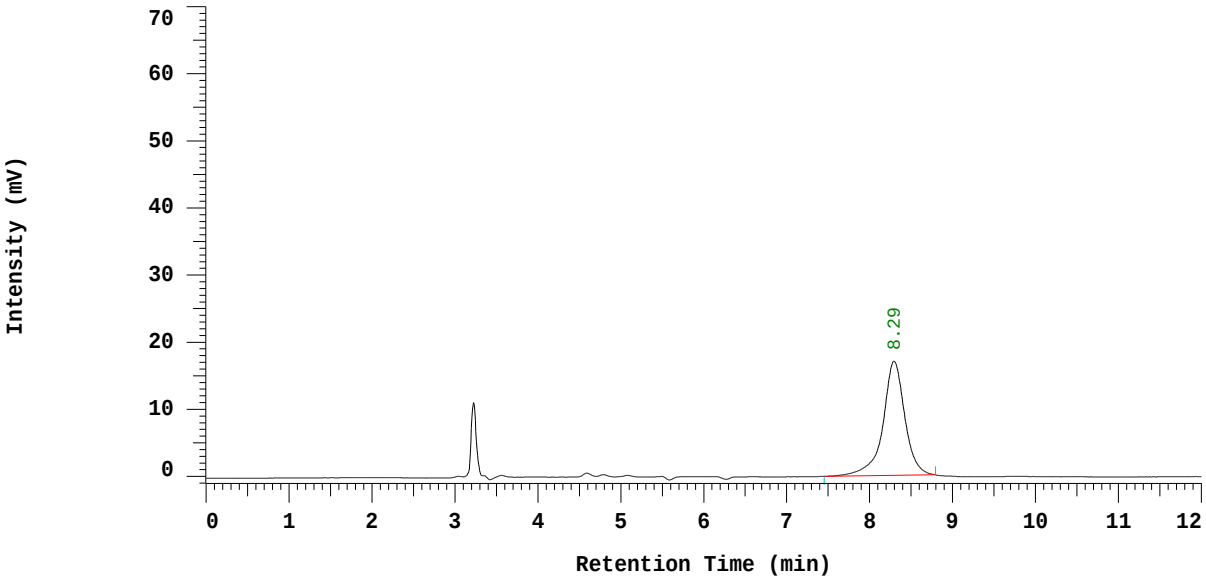
Fig S175. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 7)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 04:53 PM
Reported Date and Time: 07/01/2016 12:21 PM
Processed Date and Time: 07/01/2016 12:20 PM
Data Path: D:\Arun\DATA\0501\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0501
Application(data): Arun
Vial Number: 5
Sample Name: CHP-8g-F2 (Crys 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.29	313751	17026	100.000
		313751	17026	100.000

Peak rejection level: 5000

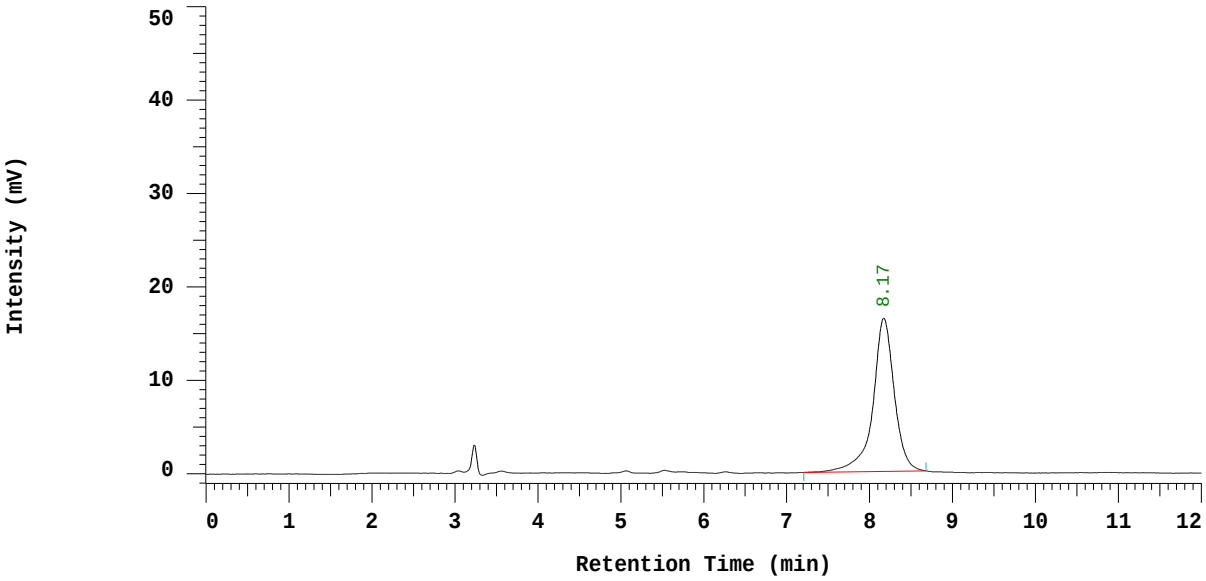
Fig S176. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 8)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 05:59 PM
Reported Date and Time: 07/01/2016 12:11 PM
Processed Date and Time: 07/01/2016 12:11 PM
Data Path: D:\Arun\DATA\0506\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0506
Application(data): Arun
Vial Number: 5
Sample Name: CHP-8g-F2 (Crys 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.17	293692	16396	100.000
		293692	16396	100.000

Peak rejection level: 5000

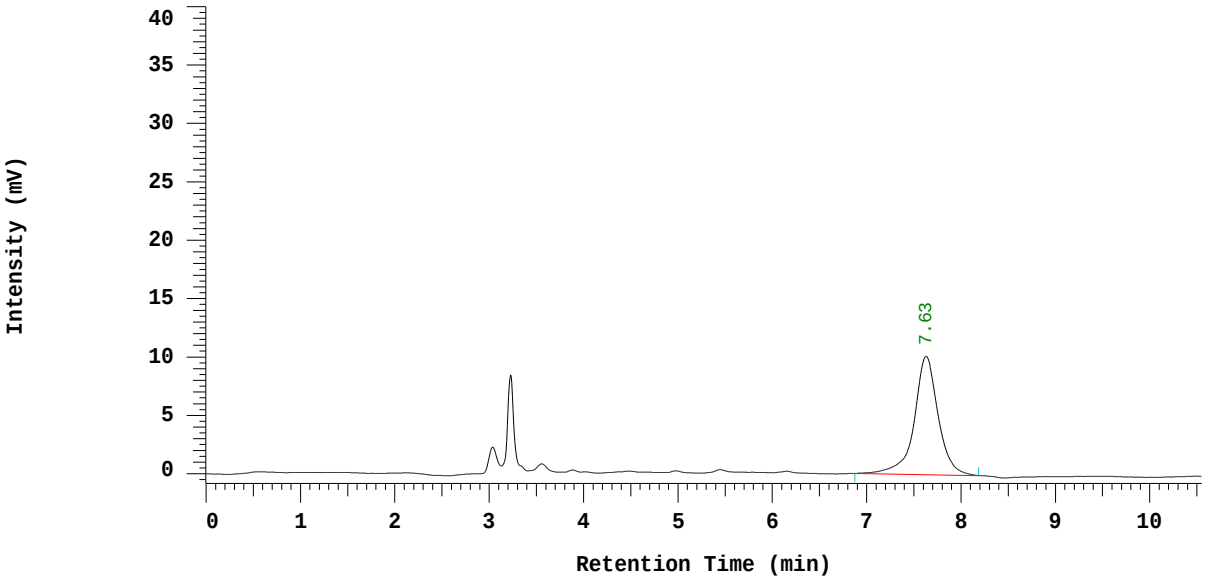
Fig S177. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 9)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 03:38 PM
Reported Date and Time: 07/01/2016 12:09 PM
Processed Date and Time: 07/01/2016 12:09 PM
Data Path: D:\Arun\DATA\0509\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0509
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	7.63	178613	10137	100.000
		178613	10137	100.000

Peak rejection level: 5000

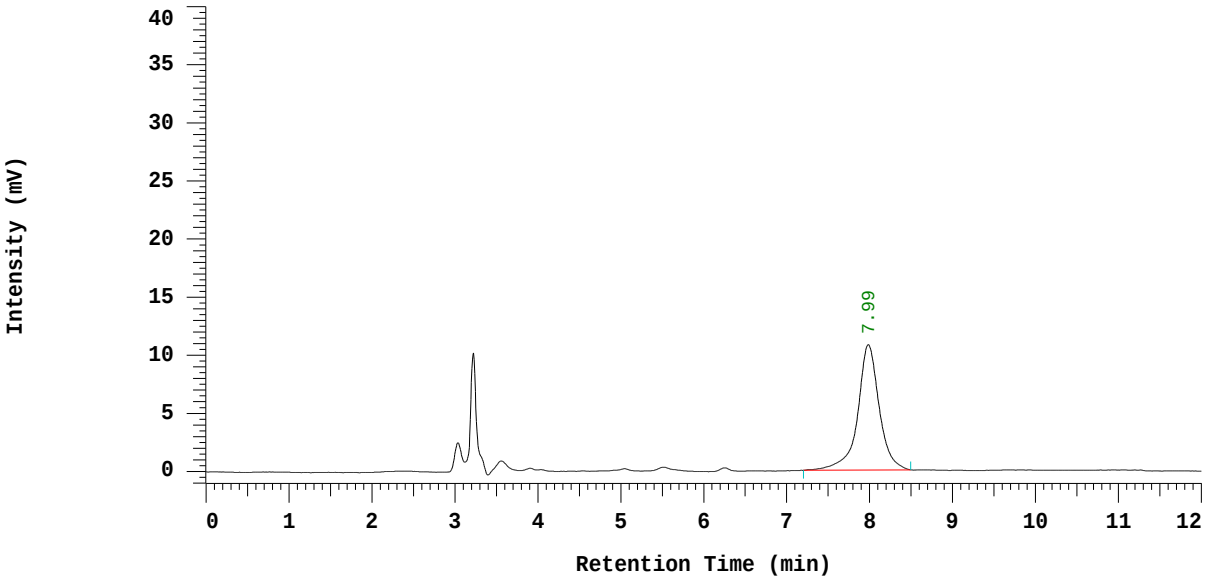
Fig S178. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 10)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 03:50 PM
Reported Date and Time: 07/01/2016 12:07 PM
Processed Date and Time: 07/01/2016 12:07 PM
Data Path: D:\Arun\DATA\0510\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0510
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	7.99	194411	10775	100.000
		194411	10775	100.000

Peak rejection level: 5000

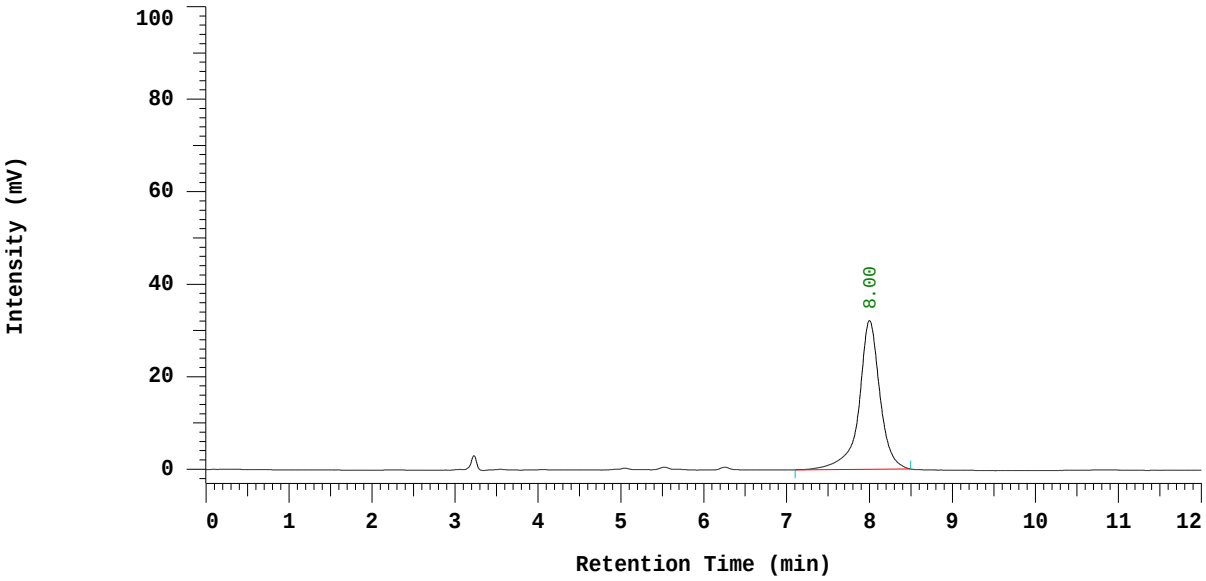
Fig S179. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 11)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 04:03 PM
Reported Date and Time: 07/01/2016 12:05 PM
Processed Date and Time: 07/01/2016 12:05 PM
Data Path: D:\Arun\DATA\0511\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0511
Application(data): Arun
Vial Number: 2
Sample Name: CHP-8g-F2 (Crys 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.00	563043	32162	100.000
		563043	32162	100.000

Peak rejection level: 5000

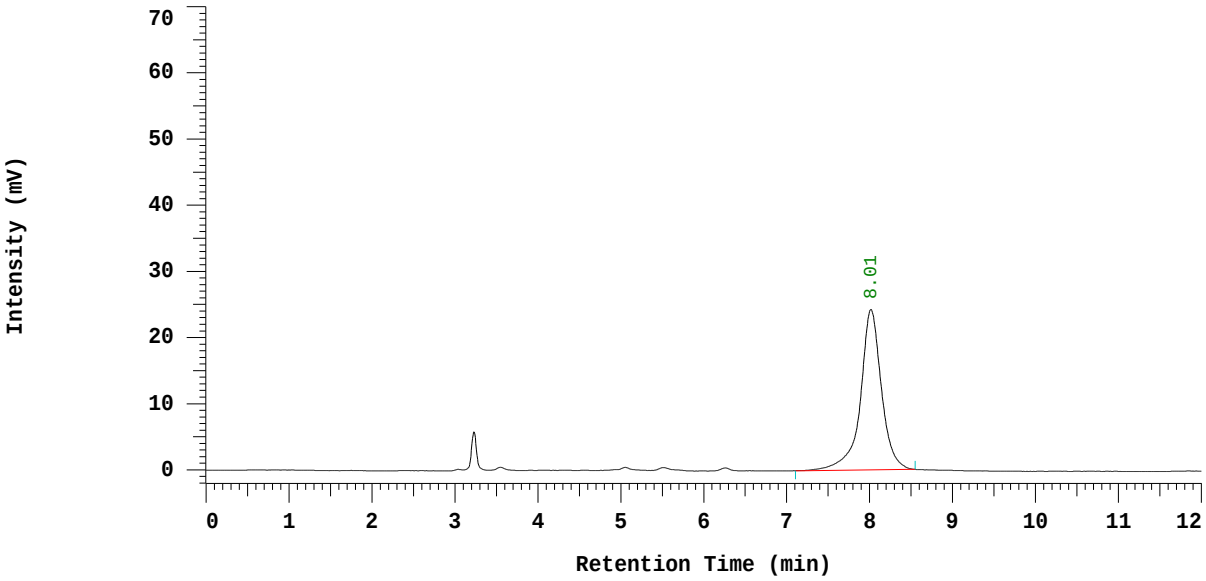
Fig S180. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 12)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 04:16 PM
Reported Date and Time: 07/01/2016 12:04 PM
Processed Date and Time: 07/01/2016 12:03 PM
Data Path: D:\Arun\DATA\0512\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0512
Application(data): Arun
Vial Number: 3
Sample Name: CHP-8g-F2 (Crys 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.01	427998	24238	100.000
		427998	24238	100.000

Peak rejection level: 5000

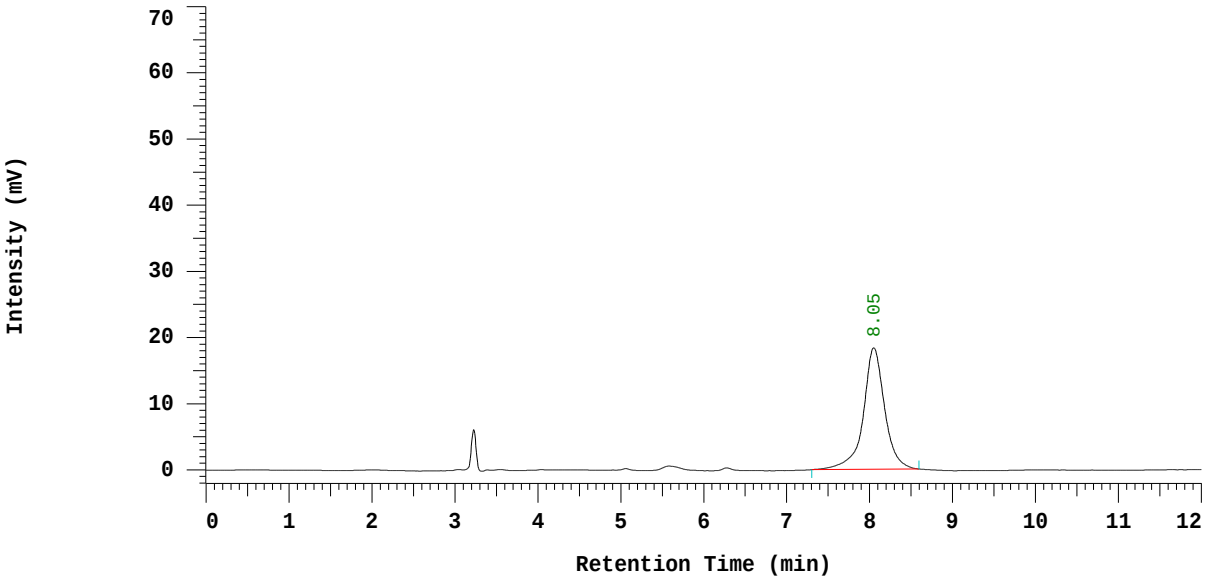
Fig S181. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 13)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 05:24 PM
Reported Date and Time: 07/01/2016 11:54 AM
Processed Date and Time: 07/01/2016 11:53 AM
Data Path: D:\Arun\DATA\0517\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0517
Application(data): Arun
Vial Number: 3
Sample Name: CHP-8g-F2 (Crys 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	8.05	328706	18358	100.000
		328706	18358	100.000

Peak rejection level: 5000

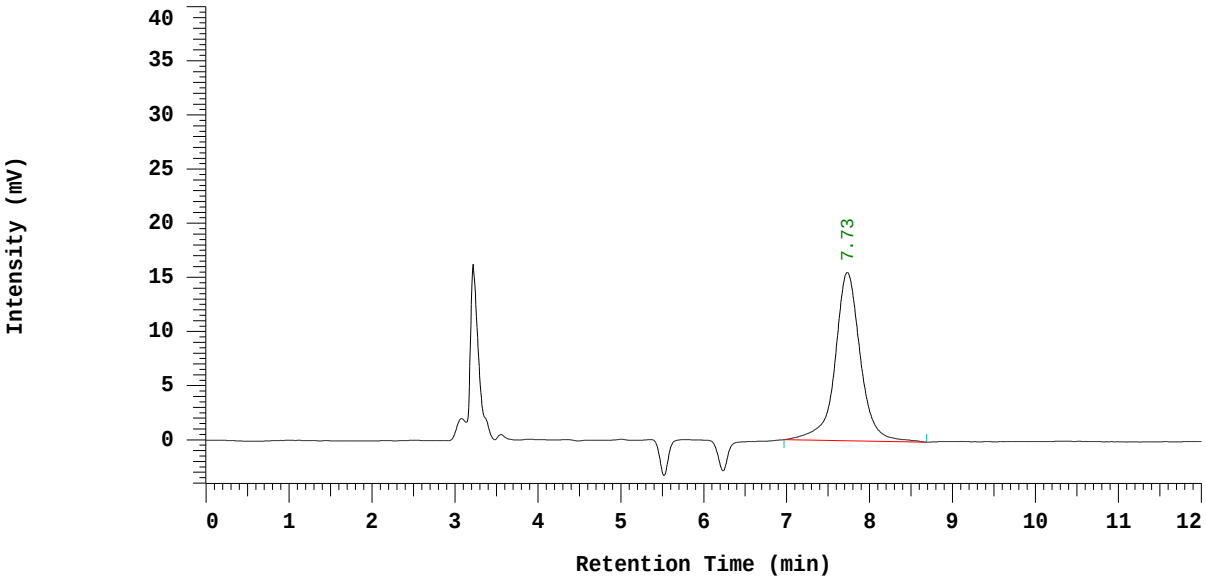
Fig S182. HPLC analysis of a crystal of the (–)-**3i** obtained (crystal count number 14)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 07/04/2016 08:13 PM
Reported Date and Time: 07/04/2016 09:13 PM
Processed Date and Time: 07/04/2016 09:12 PM
Data Path: D:\Arun\DATA\0523\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0523
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (IC18028)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	7.73	330698	15553	100.000
		330698	15553	100.000

Peak rejection level: 5000

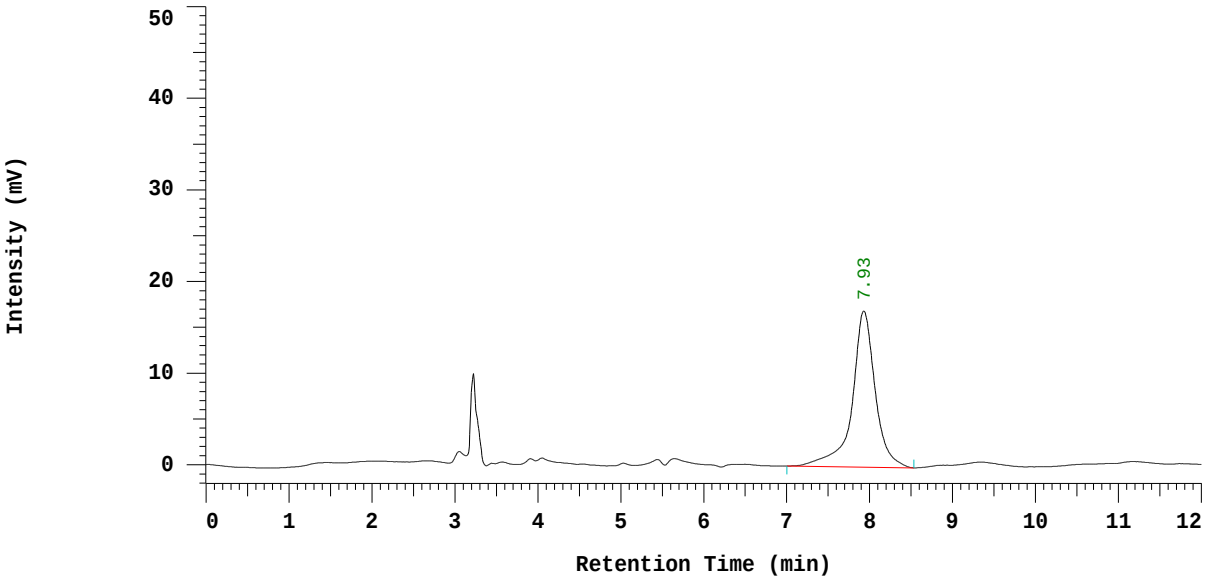
Fig S183. HPLC analysis of the crystal recovered from the X-ray analysis (IC18028, CCDC 1488798)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 07/05/2016 02:39 PM
Reported Date and Time: 07/05/2016 03:00 PM
Processed Date and Time: 07/05/2016 02:55 PM
Data Path: D:\Arun\DATA\0527\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0527
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (IC18028-Co)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	7.93	330565	17043	100.000
		330565	17043	100.000

Peak rejection level: 5000

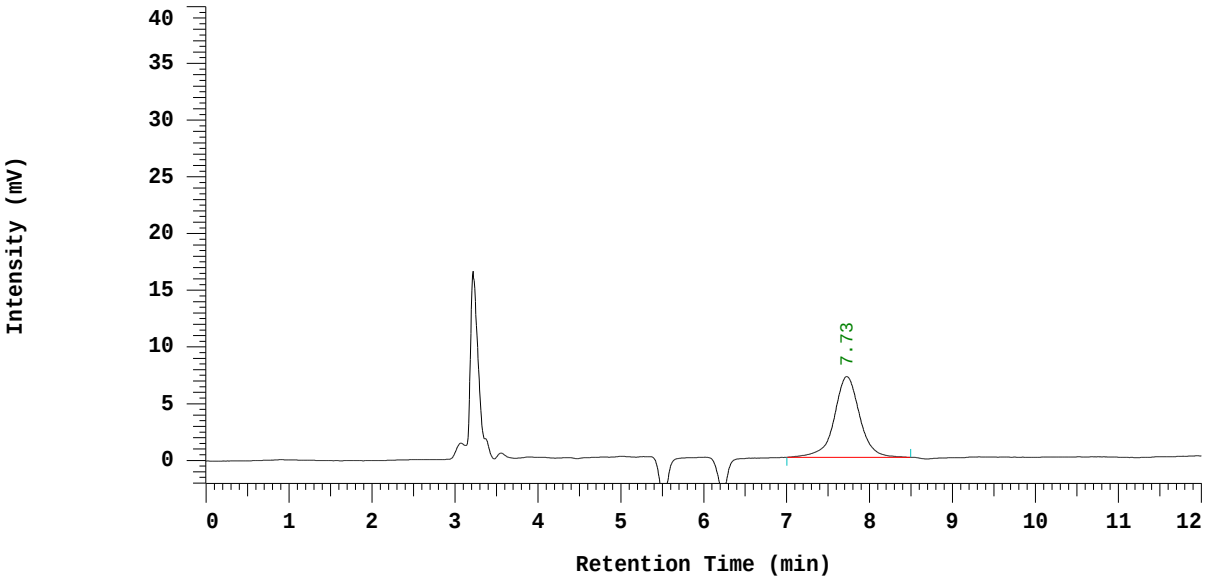
Fig S184. HPLC analysis of the co-injection of the crystal recovered from the X-ray analysis (IC18028, CCDC 1488798) and the (–)-**3i**.

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 07/04/2016 08:39 PM
Reported Date and Time: 07/04/2016 09:07 PM
Processed Date and Time: 07/04/2016 09:06 PM
Data Path: D:\Arun\DATA\0524\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0524
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (IC18028-1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	7.73	151145	7119	100.000
		151145	7119	100.000

Peak rejection level: 5000

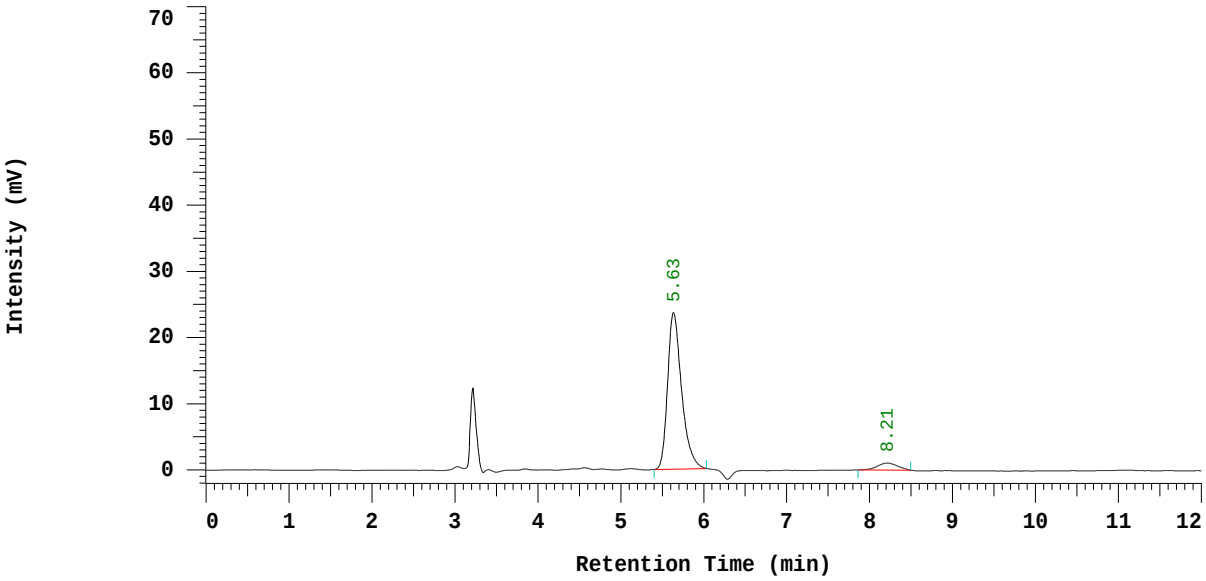
Fig S185. HPLC analysis of the crystal recovered from the X-ray analysis (IC18028-1, CCDC 1488808)

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/26/2016 04:55 PM
Reported Date and Time: 07/01/2016 12:48 PM
Processed Date and Time: 07/01/2016 12:48 PM
Data Path: D:\Arun\DATA\0484\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0484
Application(data): Arun
Vial Number: 5
Sample Name: CHP-8g-F2 (Crys 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.63	277123	23648	93.859
2	8.21	18130	1064	6.141
		295253	24712	100.000

Peak rejection level: 5000

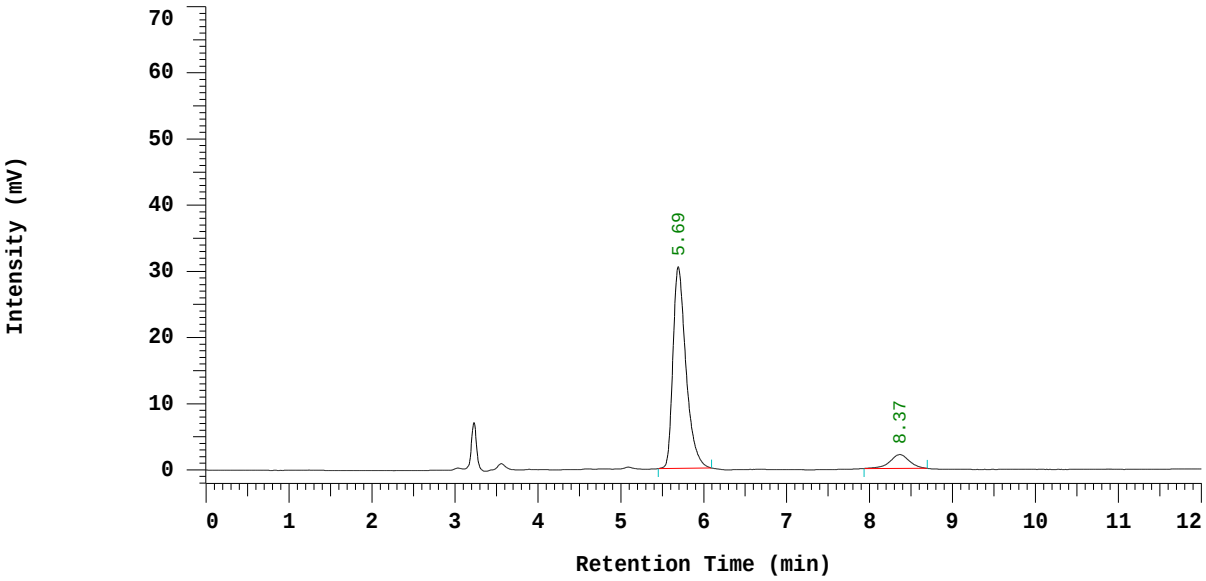
Fig S186. HPLC analysis of a crystal **3i** obtained with chiral enriched (crystal count number 1).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 05:08 PM
Reported Date and Time: 07/01/2016 12:19 PM
Processed Date and Time: 07/01/2016 12:19 PM
Data Path: D:\Arun\DATA\0502\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0502
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.69	332157	30486	90.707
2	8.37	34029	2085	9.293
		366186	32571	100.000

Peak rejection level: 5000

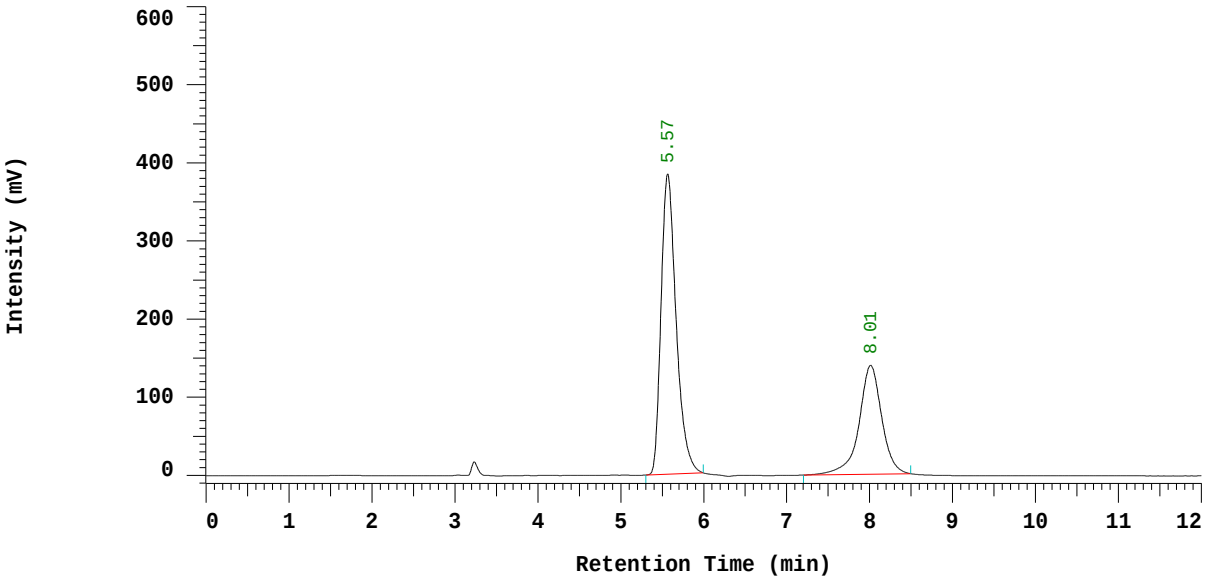
Fig S187. HPLC analysis of a crystal 3i obtained with chiral enriched (crystal count number 2).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/23/2016 05:21 PM
Reported Date and Time: 07/01/2016 01:16 PM
Processed Date and Time: 07/01/2016 01:16 PM
Data Path: D:\Arun\DATA\0467\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0467
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crystal 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.57	4845292	384221	64.647
2	8.01	2649724	139303	35.353
		7495016	523524	100.000

Peak rejection level: 5000

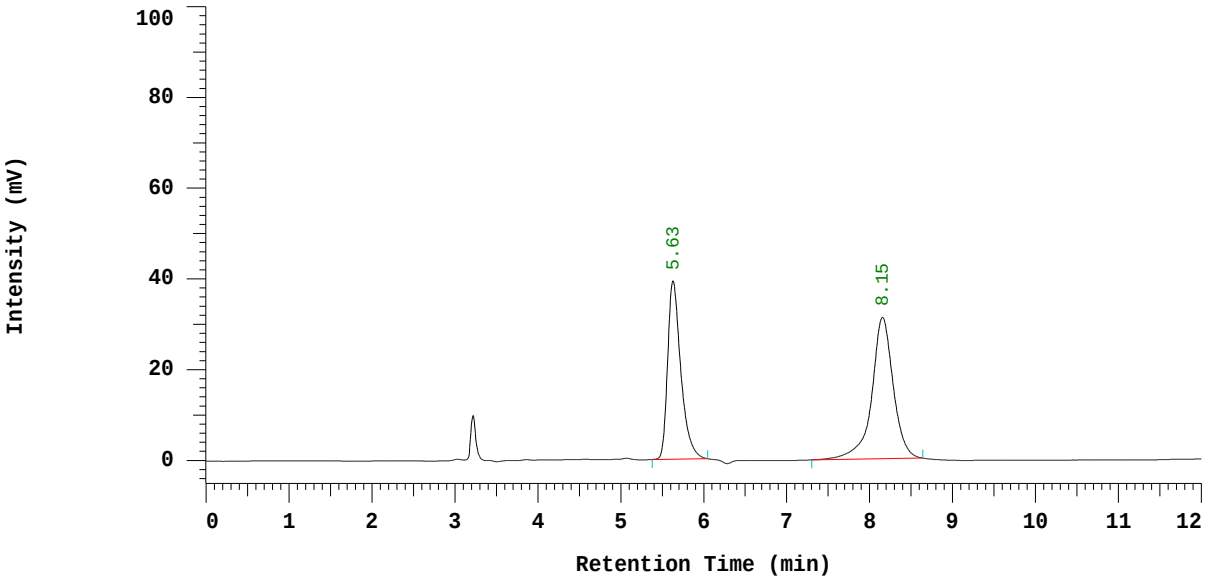
Fig S188. HPLC analysis of a crystal **3i** obtained with low ee (crystal count number 1).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/26/2016 04:41 PM
Reported Date and Time: 07/01/2016 12:50 PM
Processed Date and Time: 07/01/2016 12:50 PM
Data Path: D:\Arun\DATA\0483\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0483
Application(data): Arun
Vial Number: 4
Sample Name: CHP-8g-F2 (Crys 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.63	432836	39300	43.534
2	8.15	561421	31154	56.466
		994257	70454	100.000

Peak rejection level: 5000

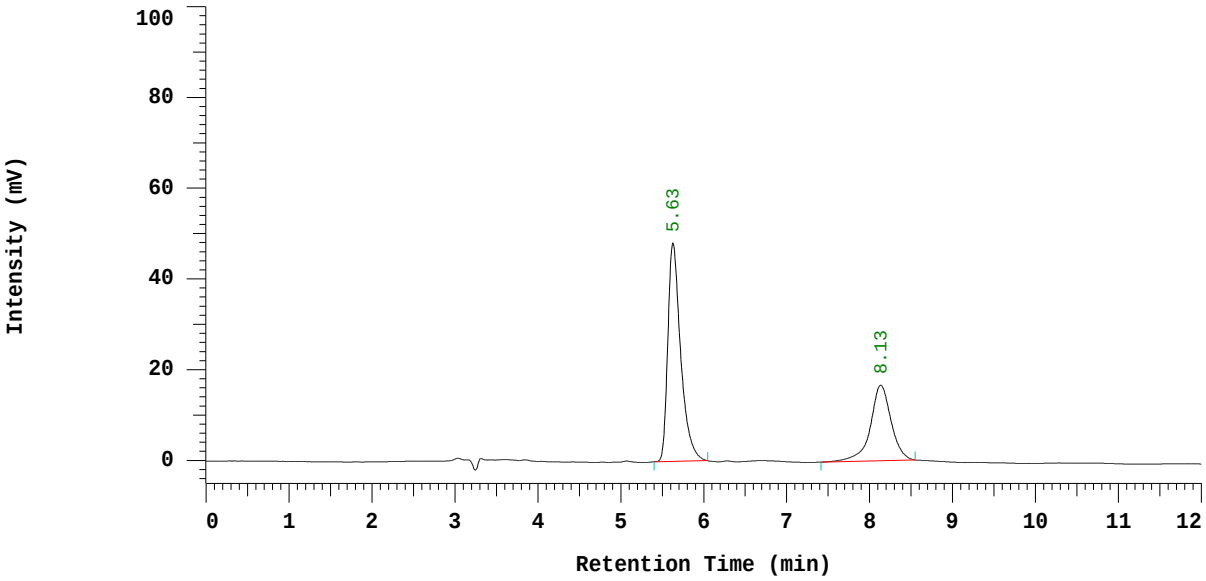
Fig S189. HPLC analysis of a crystal **3i** obtained with low ee (crystal count number 2).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 04:05 PM
Reported Date and Time: 07/01/2016 12:46 PM
Processed Date and Time: 07/01/2016 12:46 PM
Data Path: D:\Arun\DATA\0485\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0485
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.63	516846	48139	64.117
2	8.13	289258	16679	35.883
		806104	64818	100.000

Peak rejection level: 5000

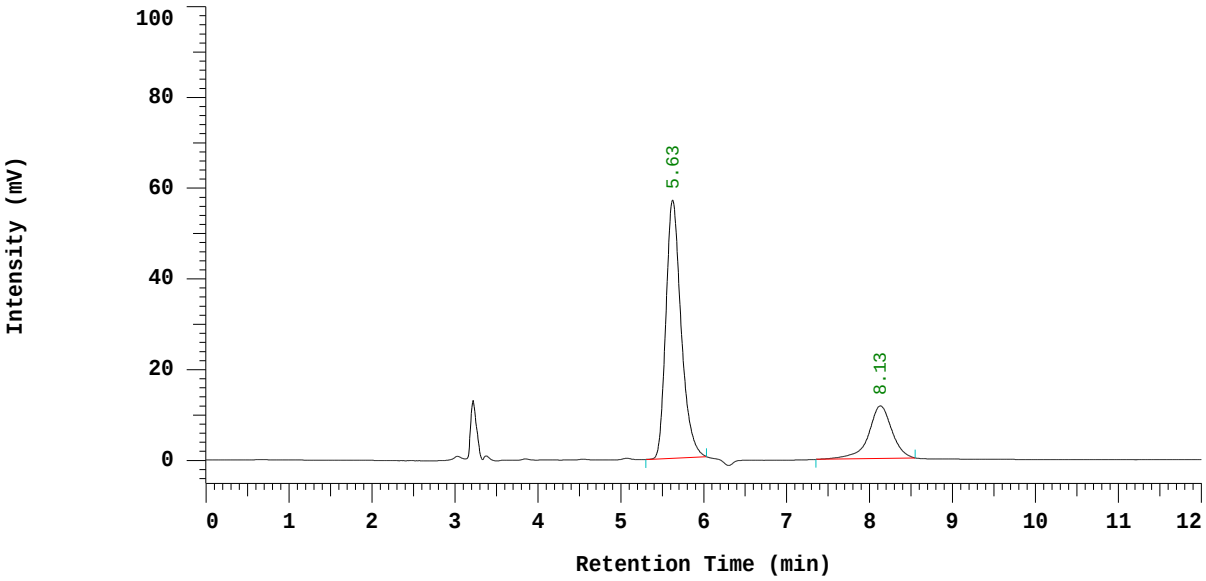
Fig S190. HPLC analysis of a crystal **3i** obtained with low ee (crystal count number 3).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 05:00 PM
Reported Date and Time: 07/01/2016 12:40 PM
Processed Date and Time: 07/01/2016 12:40 PM
Data Path: D:\Arun\DATA\0489\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0489
Application(data): Arun
Vial Number: 5
Sample Name: CHP-8g-F2 (Crys 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.63	723288	56910	76.120
2	8.13	226909	11587	23.880
		950197	68497	100.000

Peak rejection level: 5000

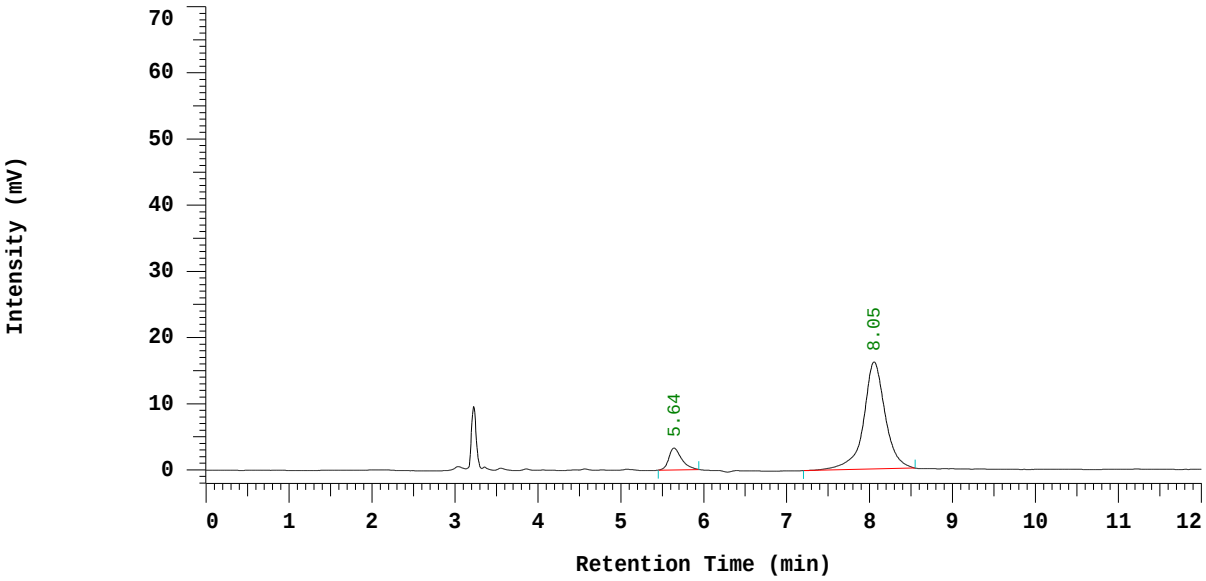
Fig S191. HPLC analysis of a crystal **3i** obtained with low ee (crystal count number 4).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 05:48 PM
Reported Date and Time: 07/01/2016 12:34 PM
Processed Date and Time: 07/01/2016 12:34 PM
Data Path: D:\Arun\DATA\0492\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0492
Application(data): Arun
Vial Number: 3
Sample Name: CHP-8g-F2 (Crys 3)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.64	35093	3289	10.672
2	8.05	293735	16188	89.328
		328828	19477	100.000

Peak rejection level: 5000

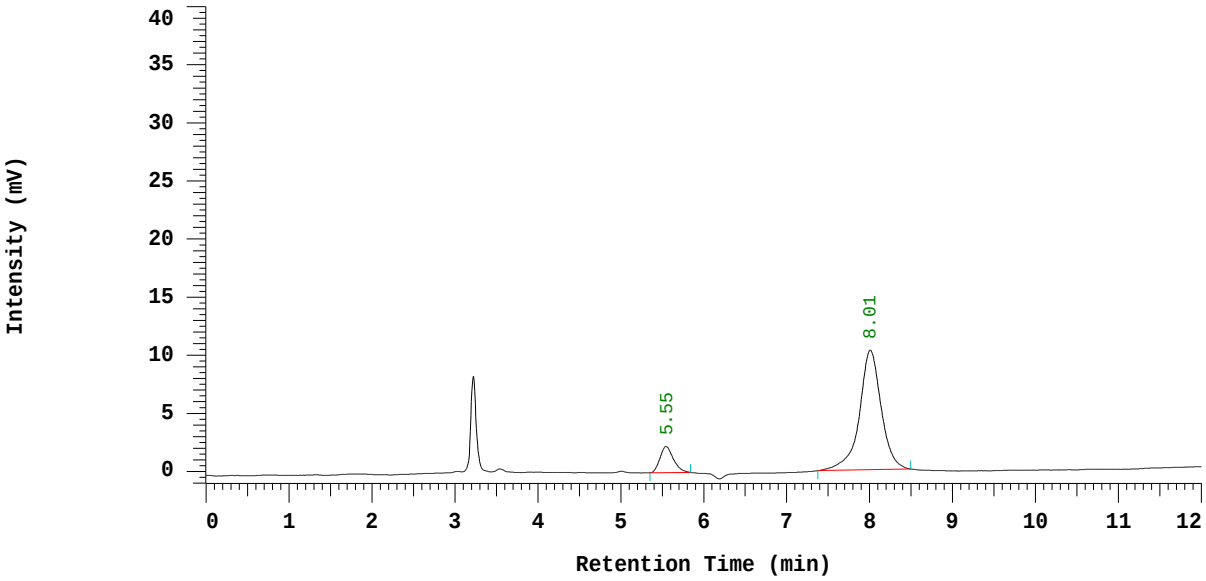
Fig S192. HPLC analysis of a crystal **3i** obtained with low ee (crystal count number 5).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 04:01 PM
Reported Date and Time: 07/01/2016 12:27 PM
Processed Date and Time: 07/01/2016 12:27 PM
Data Path: D:\Arun\DATA\0497\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0497
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.55	25275	2257	11.866
2	8.01	187727	10277	88.134
		213002	12534	100.000

Peak rejection level: 5000

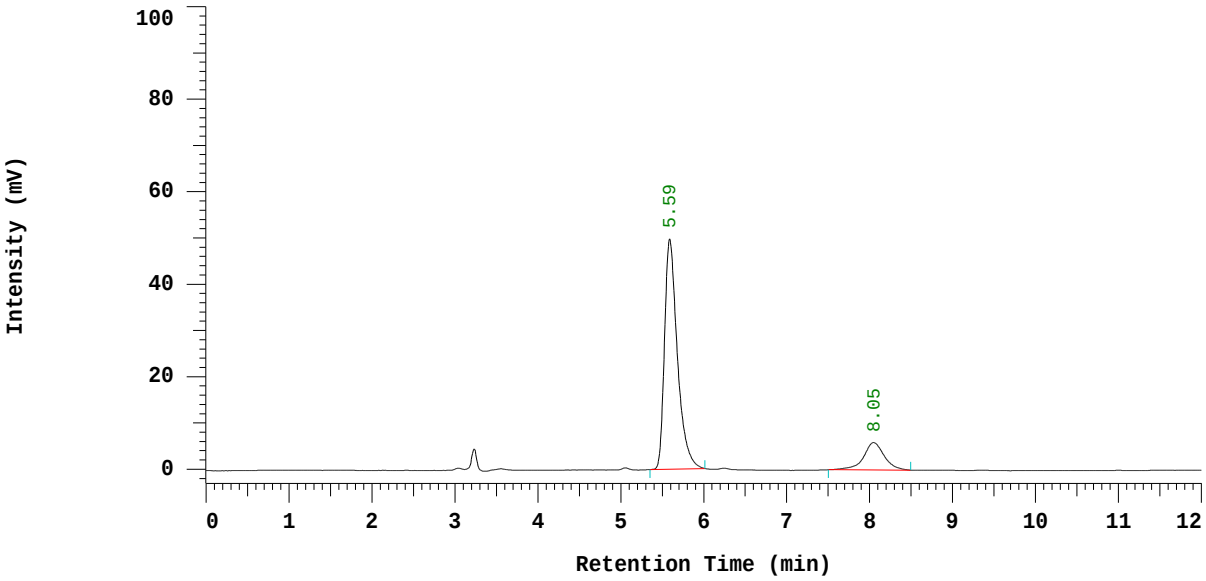
Fig S193. HPLC analysis of a crystal **3i** obtained with low ee (crystal count number 6).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 04:30 PM
Reported Date and Time: 07/01/2016 12:02 PM
Processed Date and Time: 07/01/2016 12:01 PM
Data Path: D:\Arun\DATA\0513\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0513
Application(data): Arun
Vial Number: 4
Sample Name: CHP-8g-F2 (Crys 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.59	534229	49723	83.775
2	8.05	103463	5932	16.225
		637692	55655	100.000

Peak rejection level: 5000

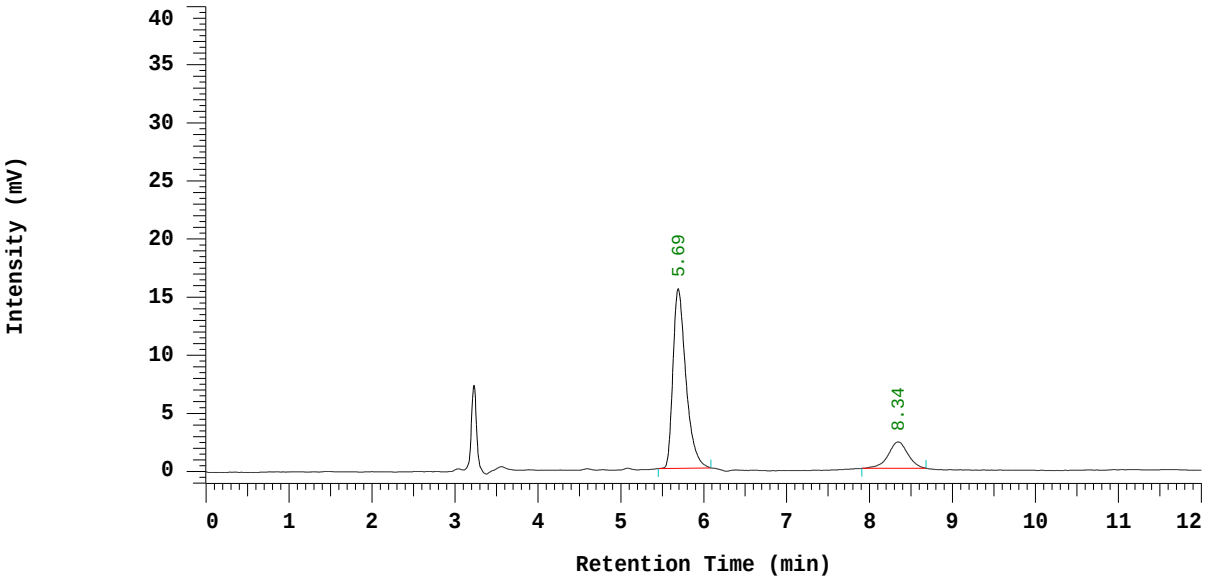
Fig S194. HPLC analysis of a crystal **3i** obtained with low ee (crystal count number 7).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/29/2016 05:21 PM
Reported Date and Time: 07/01/2016 12:17 PM
Processed Date and Time: 07/01/2016 12:17 PM
Data Path: D:\Arun\DATA\0503\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0503
Application(data): Arun
Vial Number: 2
Sample Name: CHP-8g-F2 (Crys 2)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.69	167329	15446	81.733
2	8.34	37396	2266	18.267
		204725	17712	100.000

Peak rejection level: 5000

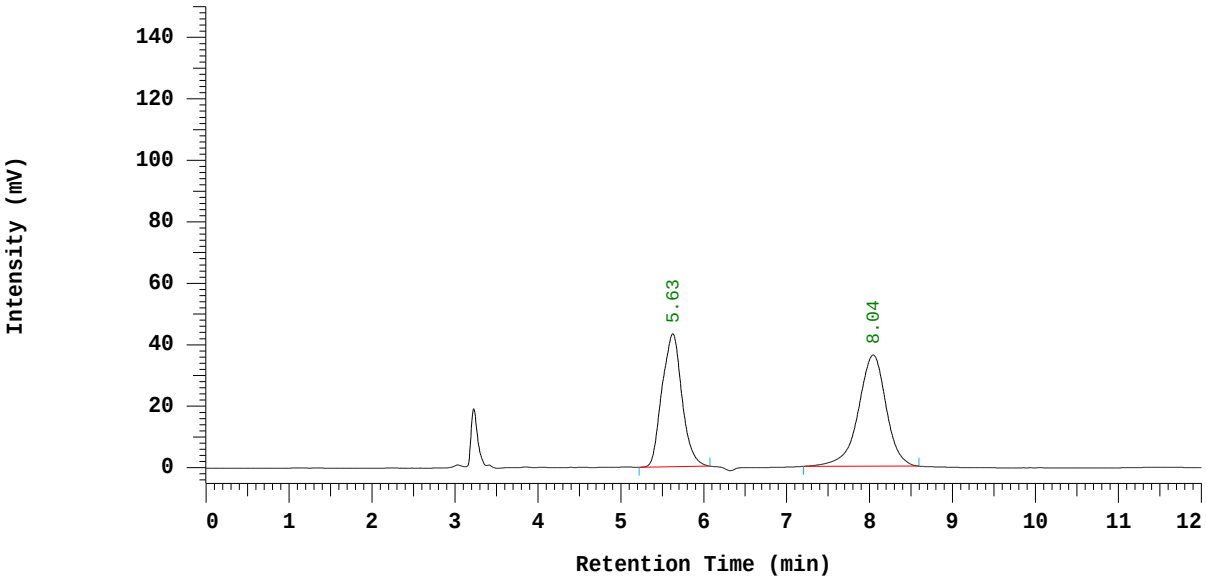
Fig S195. HPLC analysis of a crystal **3i** obtained with low ee (crystal count number 8).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/24/2016 01:17 PM
Reported Date and Time: 07/01/2016 01:00 PM
Processed Date and Time: 07/01/2016 01:00 PM
Data Path: D:\Arun\DATA\0478\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0478
Application(data): Arun
Vial Number: 5
Sample Name: CHP-8g-F2 (Crys 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.63	721768	43285	46.139
2	8.04	842566	36161	53.861
		1564334	79446	100.000

Peak rejection level: 5000

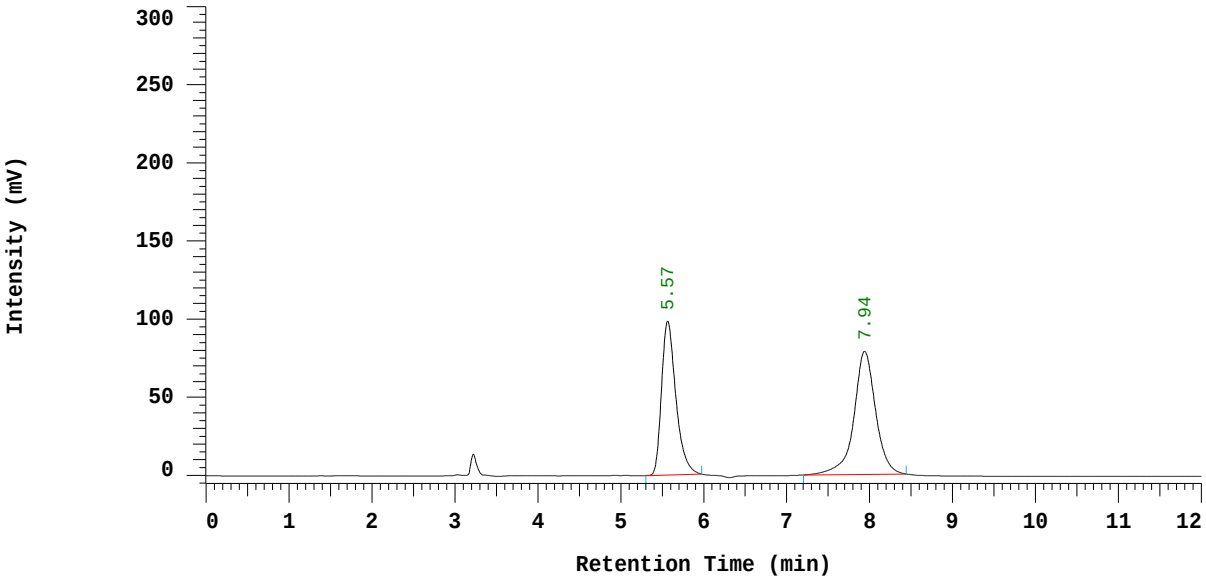
Fig S196. HPLC analysis of a crystal **3i** obtained with very low ee (crystal count number 1).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/23/2016 06:11 PM
Reported Date and Time: 07/01/2016 01:12 PM
Processed Date and Time: 07/01/2016 01:11 PM
Data Path: D:\Arun\DATA\0470\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0470
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crystal 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.57	1180654	98373	45.116
2	7.94	1436277	78794	54.884
		2616931	177167	100.000

Peak rejection level: 5000

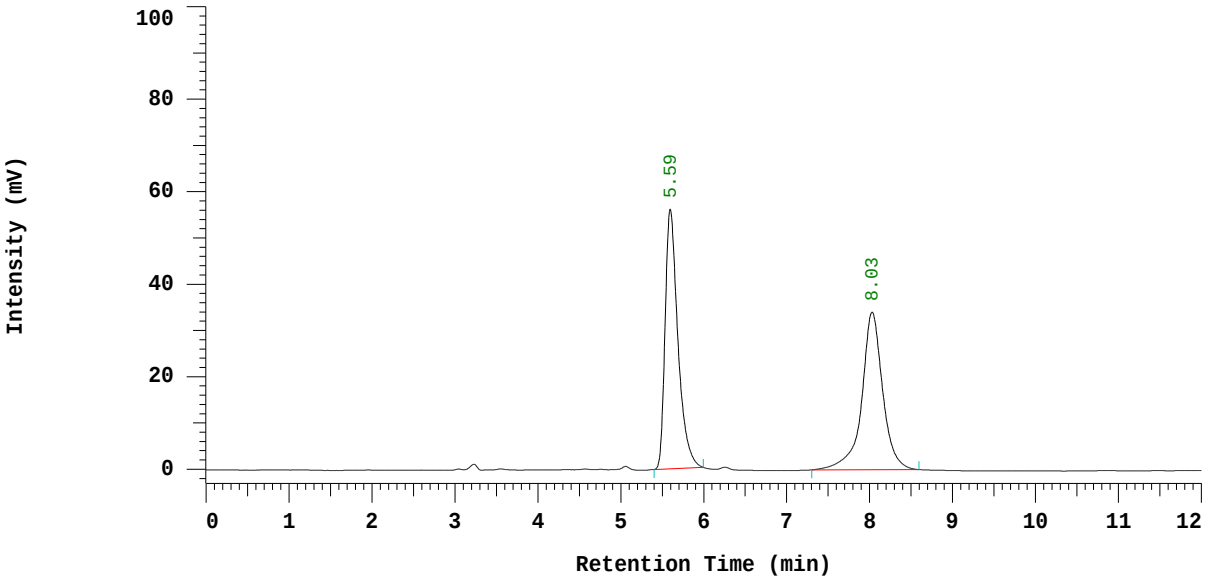
Fig S197. HPLC analysis of a crystal **3i** obtained with very low ee (crystal count number 2).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 04:42 PM
Reported Date and Time: 07/01/2016 12:00 PM
Processed Date and Time: 07/01/2016 12:00 PM
Data Path: D:\Arun\DATA\0514\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0514
Application(data): Arun
Vial Number: 5
Sample Name: CHP-8g-F2 (Crys 5)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.59	600148	56147	50.073
2	8.03	598406	34061	49.927
		1198554	90208	100.000

Peak rejection level: 5000

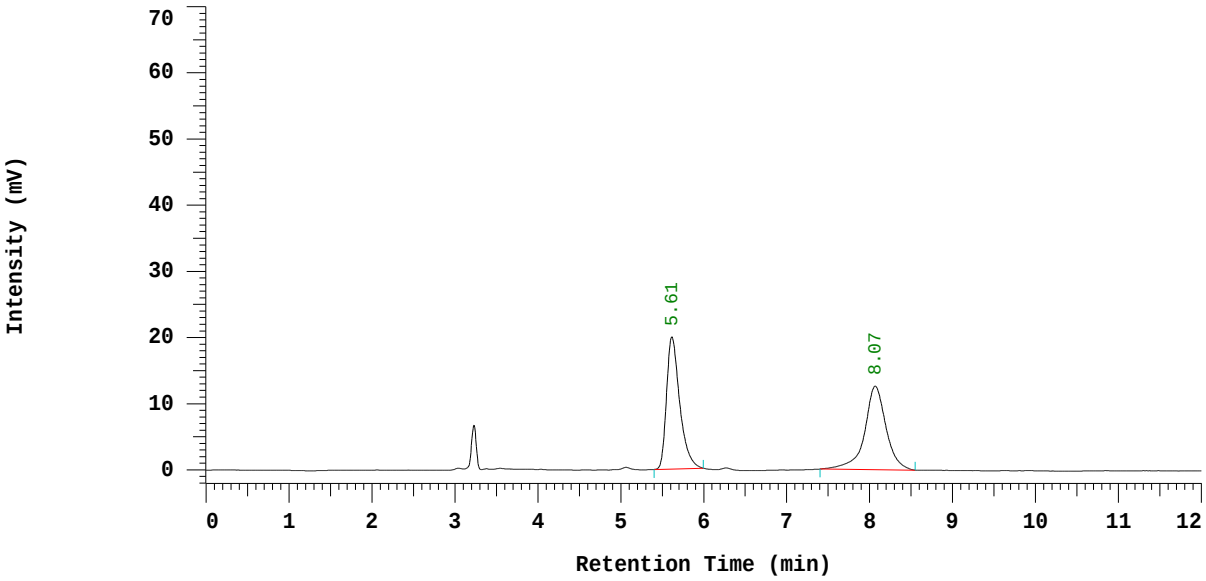
Fig S198. HPLC analysis of a crystal **3i** obtained with racemic mixture (crystal count number 1).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/30/2016 05:37 PM
Reported Date and Time: 07/01/2016 11:52 AM
Processed Date and Time: 07/01/2016 11:51 AM
Data Path: D:\Arun\DATA\0518\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0518
Application(data): Arun
Vial Number: 4
Sample Name: CHP-8g-F2 (Crys 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.61	220086	19960	49.292
2	8.07	226410	12632	50.708
		446496	32592	100.000

Peak rejection level: 5000

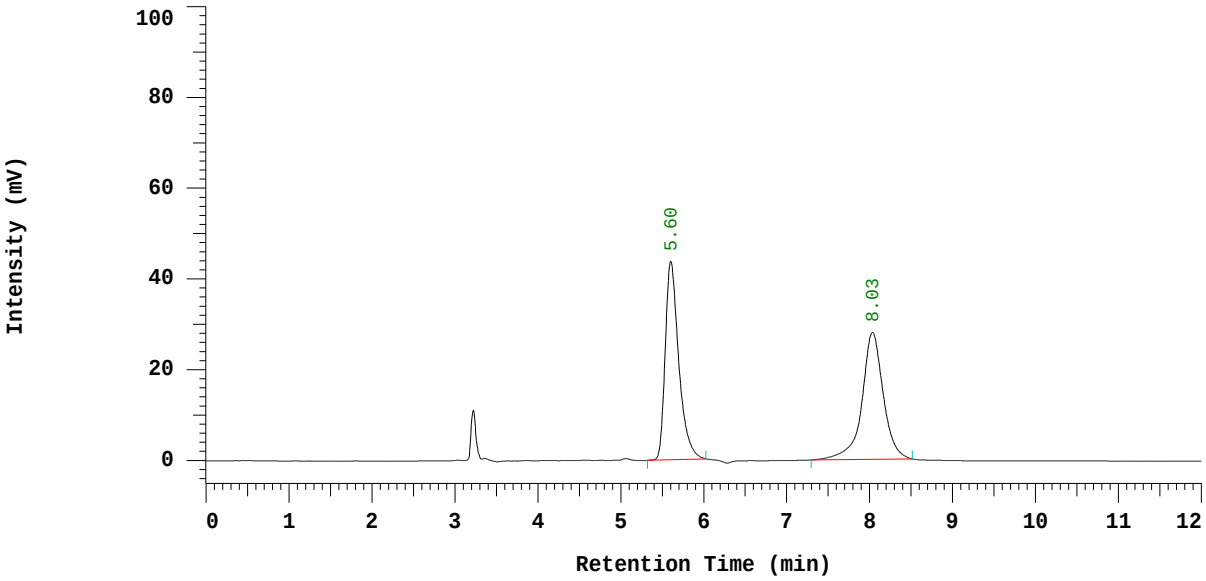
Fig S199. HPLC analysis of a crystal **3i** obtained with racemic mixture (crystal count number 2).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/27/2016 05:22 PM
Reported Date and Time: 07/01/2016 12:38 PM
Processed Date and Time: 07/01/2016 12:37 PM
Data Path: D:\Arun\DATA\0490\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0490
Application(data): Arun
Vial Number: 1
Sample Name: CHP-8g-F2 (Crys 1)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.60	493609	43720	49.641
2	8.03	500748	27998	50.359
		994357	71718	100.000

Peak rejection level: 5000

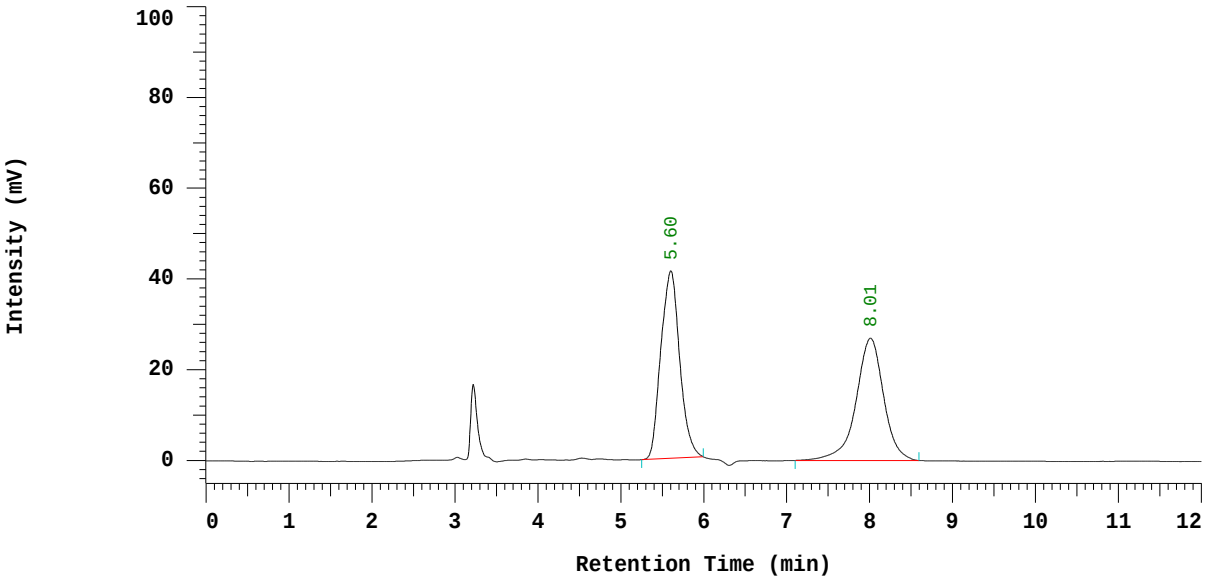
Fig S200. HPLC analysis of a crystal **3i** obtained with racemic mixture (crystal count number 3).

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 06/24/2016 01:04 PM
Reported Date and Time: 07/01/2016 01:03 PM
Processed Date and Time: 07/01/2016 01:03 PM
Data Path: D:\Arun\DATA\0477\
Processing Method: test-THF/Hx-Final II

System (acquisition): Sys 1
Series: 0477
Application(data): Arun
Vial Number: 4
Sample Name: CHP-8g-F2 (Crys 4)
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: 25%THF+HX 1.0 mL/MIN COL-IC

Chrom Type: Fixed WL Chromatogram, 254 nm



Processing Method: test-THF/Hx-Final II
Column Type: IC
Method Developer: ARUN
Method Description:

Chrom Type: Fixed WL Chromatogram, 254 nm
Peak Quantitation: AREA
Calculation Method: EXT-STD
Scale Factor 1: 1.000

No.	RT	Area	Height	Area %
1	5.60	650641	41299	51.122
2	8.01	622071	26912	48.878
		1272712	68211	100.000

Peak rejection level: 5000

Fig S201. HPLC analysis of a crystal **3i** obtained with racemic mixture (crystal count number 4).